INORGANIC CHEMISTRY

TARGET CSIR NET

PREVIOUS YEAR SOLUTION'S

QUANTA
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Coordination Chemistry

Hints & Solutions

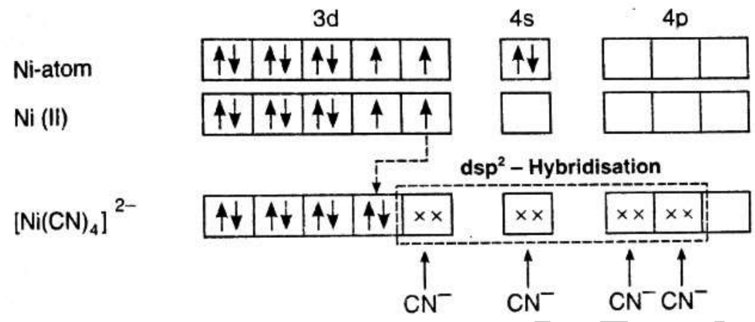
Explanations:

1) c

In, **$Ni(CN_4)^{2-}$** oxidation state of Ni is +2 & its valence shell electronic configuration is $3d^8$ .Since CN^- is a strong ligand ,therefore these ligands cause to pair up two unpaired electron ,resulting in vacant 3d orbital .

Hybridization: dsp2

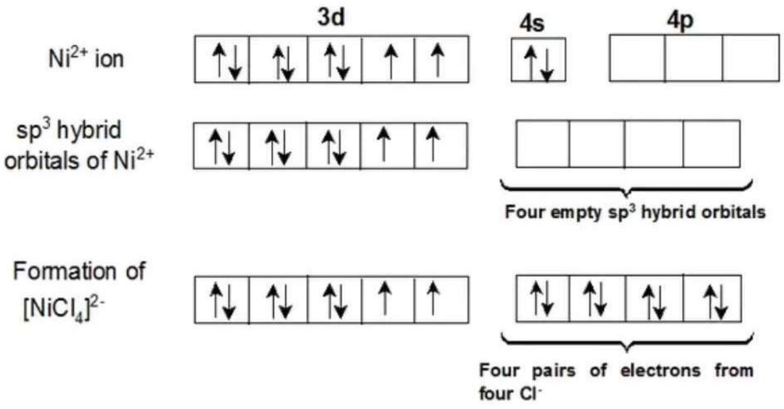
Geometry: Square planar.



In **$Ni(Cl_4)^{2-}$,** oxidation state of Ni is +2 & its valence shell electronic configuration is $3d^8$ Since Cl^- is a weak ligand , no pairing ,none of the 3d orbital is vacant .

Hybridization: sp^3

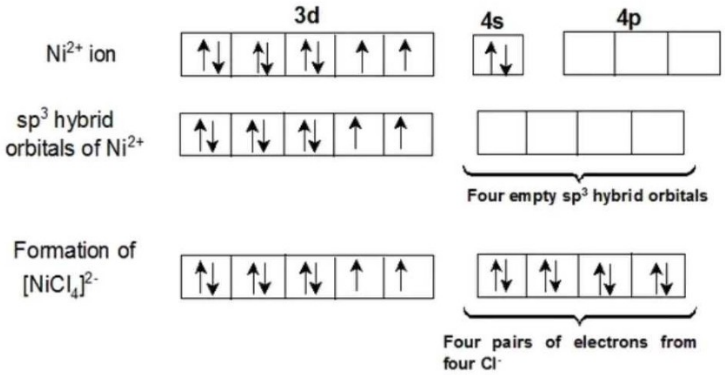
Geometry: tetrahedral


3d
4s
4p
Ni²⁺ ion
sp³ hybrid orbitals of Ni²⁺
Four empty sp³ hybrid orbitals
Formation of [NiCl₄]²⁻
Four pairs of electrons from four Cl⁻

2) c

Oxidation state of Ni is +2 & its valence shell electronic configuration $3d^8$

For two unpaired electrons geometry is **Tetrahedral.**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3) b

For term symbol only valence shell is considered.

Term symbol $^{2s+1}L_{g/u}^{+/-}$

S = ½+½ =1 , 2s+1= 3

L= 1x(1)+ 1x(-1) = 0 , the term symbol is ∑

When molecular orbital is π , 2s+1= 3 give negative sign to distinguish ∑ terms

g and u are used for molecules which have COS present , u*u =g

4) a

HOMO= σ* of Cr^{+2}	HOMO= σ* of Cr^{+2}
LUMO= σ* of Co^{+3}	LUMO= π/π* of Ru^{+3}
Acceleration =10^{10}	Acceleration =10^{2}

Inner sphere mechanism is favourable for σ→σ* transition only.

5) d

For a d^5 octahedral complex $[Mn(H_2O)_6]^{+2}$ all transitions are Laporte forbidden (orbital forbidden) as well as spin forbidden. Absorptions associated with doubly forbidden transitions are extremely weak, so it is very lightly coloured.

6) a

In the given case ligand in same, so higher the formal oxidation state of the metal , lower will be LMCT.

Mn	Oxidation state +7
Cr	Oxidation state +6
V	Oxidation state +5

So, order is $\mathbf{MnO_4^- < CrO_4^{2-} < VO_4^{3-}}$

7) d

a) $Ni^{+2} = 3d^8$, No Jahn - Teller distortion , ideal Oh
b) $Mn^{+2} = 3d^5$, No Jahn - Teller distortion , ideal Oh
c) $Cr^{+3}= 3d^3$, No Jahn - Teller distortion , ideal Oh
d) $Ti^{+3}= 3d^1$, shows Jahn - Teller distortion , ideal Oh geometry is not observed

8) b

For ^3D

2S+1 = 3, 2S=2, S=1
S=1, L=2
For term, S, P, D, F
Value of L= 0, 1, 2, 3
J can have values from [L+S].....[L-S]
|2-1 |.....|2+1|
3 2 1
Possible J Values are : 3

9) b

Charge transfer spectra are possible due to transfer of electron from ligand to metal or from metal to ligand.

In **Ceric ammonium nitrate** $(NH_4)_2 [Ce(NO_3)_6]$, metal is in a high oxidation state & ligand has reducing properties undergo ligand to metal charge transfer.So, Intense colour of Ceric ammonium nitrate, $(NH_4)_2 [Ce(NO_3)_6]$ is due to charge transfer from bidentate NO^{-3} to Ce^{+4} which has C.N= 12.

10) c

Kurnakov test is used to distinguish between cisplatin and transplatin, by using thiourea as a reagent.

Cisplatin+ Aqueous thiourea → deep yellow solution and on crystallisation it gives yellow needle shape crystal of tetrakis(thiourea) platinum (II) chloride

Transplatin + aqueous thiourea →Colourless solution on crystallisation it gives white needle shape crystal of trans-bis(thiourea)diaammine platinum (II) chloride

11) b

Total isomers = geometrical isomer + ½(optical isomer)
Geometrical isomer = 2 isomers (trans form + cis form)
Optical isomer = 2 isomers (d –cis-form + l-cis form)
Total isomers= 3

12) d

N→ $1s^1 2s^2 2p^3$
L=1+ 0 -1= 0
s=3/2
2s+1=2x3/2+1=4
J=(L+S).... (L-S)
=|0+3/2|.... |0-3/2|= 3/2
Therefore, Ground state term = S
Term symbol = $^4S_{3/2}$

13) c

$\mathbf{[Co(NH_3)_6]^{3+}}$ highest value of Δ_0
Highest energy (v) or lowest value of wavelength is absorbed

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14) b

Number of unpaired electrons = 2.

Thus this complex is tetrahedral. Tetrahedral complexes show only one isomer. Magnetic moment corresponding to two unpaired electrons 2.9 B.M. The hesh values 3.20 due to spin-orbit coupling.

15) b

For allowed transition : a)Spin multiplicity should be same or $\Delta S = 0$

Therefore (a) is not allowed as $\Delta S \neq 0$

b) $\Delta L = 0, \pm$,1for allowed transition

Therefore (c) is not allowed as $\Delta L \neq 0, \pm$ 1

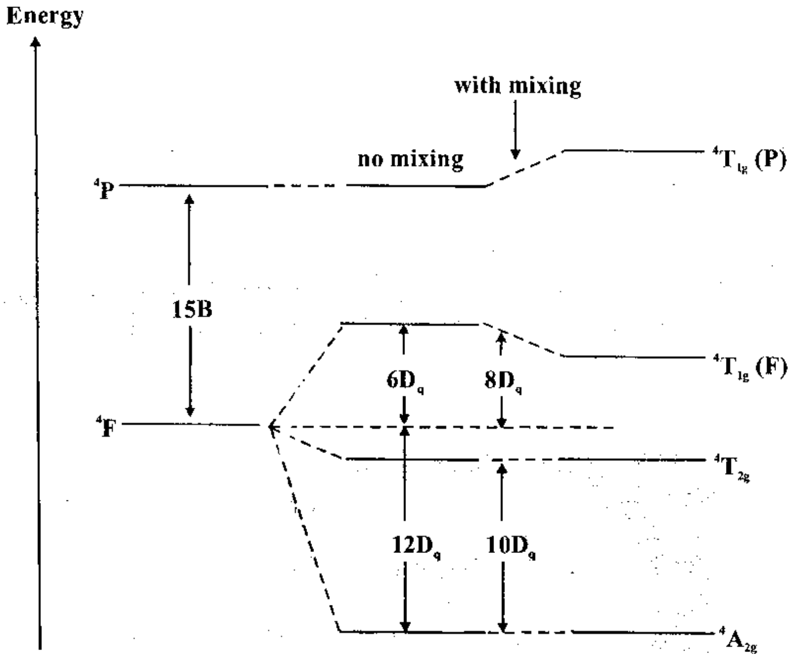
c) u → g (allowed)

g→ g (not allowed)

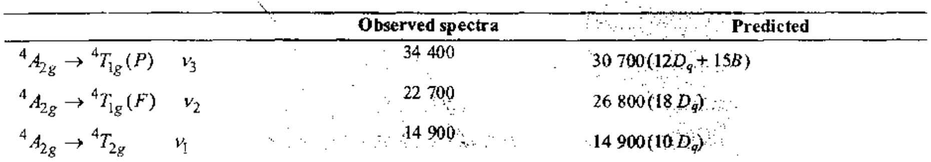
Therefore (b) is correct option.

16) b

For d^3 and d^8 , the lowest transition gives the value of $\mathbf{\Delta_o}$



Correlation of spectra for $[CrF_6]^{3-}$ (in cm^{-1})



	Observed spectra	Predicted
$^4A_{2g} \rightarrow {}^4T_{1g}(P)$ ν_3	34 400	30 700(12D_q + 15B)
$^4A_{2g} \rightarrow {}^4T_{1g}(F)$ ν_2	22 700	26 800(18 D_q)
$^4A_{2g} \rightarrow {}^4T_{2g}$ ν_1	14 900	14 900(10 D_q)

17) b

Substitution nucleophilic unimolecular conjugate base mechanism.

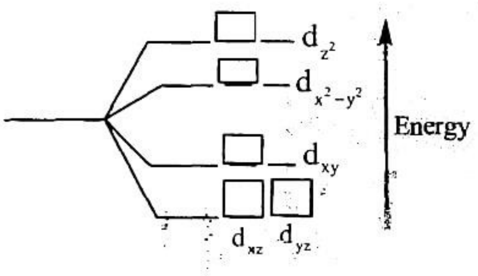
$[CoCl(NH_3)_5]^{+2} + OH^- \rightarrow [Co(NH_3)_4(NH_2)Cl]^{+1} + H_2O$

$[Co(NH_3)_4(NH_2)Cl]^{+1} \xrightarrow{\text{`ab} \quad \text{cde}} [Co(NH_3)_4(NH_2)]^{+2} + Cl^{-1}$

$[Co(NH_3)_4(NH_2)]^{+2} + OH^- \rightarrow [Co(NH_3)_5OH]^{+2}$

18) d

Explanation



.

19) c

$[Co^*(NH_3)_6]^{+2}$→High spin
$[Co^*(NH_3)_6]^{+3}$ →Low spin
$[Ru(NH_3)_6]^{+2}$→ Low spin ;
$[Ru^*(NH_3)_6]^{+3}$ →Low spin

20) d

For Ce^{+4} ions NO_3^- behaves as bidentate ligand. Thus C.N. for $\mathbf{[Ce(NO_3)_6]^{-2}}$ is 12 and shape corresponding to C.N=12 is icosahedron**.**

21) c

Ligand Cl^- is both **σ**-donor and **π** donor

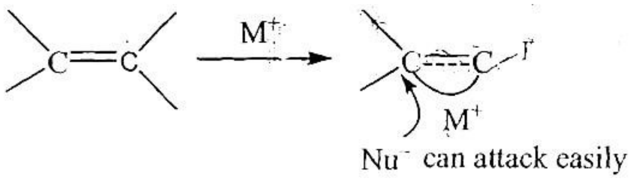
According to LFT, each ligand is always a **σ** -donor some ligands like: NH_3 which has only one lone pair of electrons is only **σ** -donor. Some ligands like F^-, Cl^-, OH^- etc. which hence two or more lone pair of electrons are **σ** as well as **π** donors. Some ligands like CO, CN^-, SH_4, bpy, phen, etc. have **π*** vacant -orbitals so these are **σ** -donor but **π**- acceptors.

22) c

Spin-orbit coupling of d-electrons takes place in which $\mathbf{t_{2g}}$ orbitals are unsymmetrically filled.

23) d

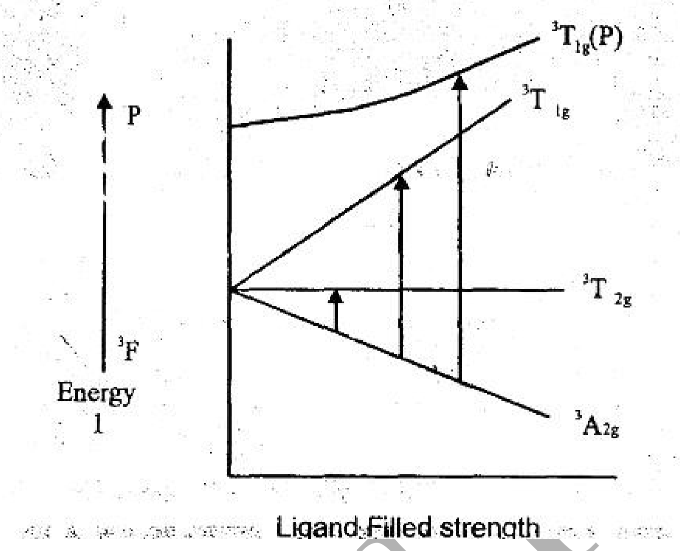
Nucleophilic attack on olefins under mild conditions



So, it requires activation by coordination to metal.

24) b

For Ni^{+2} ion in free state, the thus having same spin multiplicity as ^3F and ^3P. In octahedral field, ^3F splits into $^3A_{2g}$, $^3T_{2g}$ and $^3T_{1g}$ terms but ^3P does not split but it transforms into $^3T_{1g}$ (P). Therefore orgel diagram is.



Three electronic transitions are $^3T_{2g} \leftarrow {}^3A_{2g}$, $^3T_{1g} \leftarrow {}^3A_{2g}$, $^3T_{1g}$ (P) $\leftarrow {}^3A_{2g}$

25) c

We know that number of microstates= $\frac{f!}{h!(f\$h)!}$

For d^5, r= 5, l=2 Therefore,

n = 2(2l+1)= 2(2x2+1) = 10

Number of microstates = $\frac{}{k!\times k!} = 252 = 7\times 6^{q}$

ij!

26) c

For allowed transition :

(a) Spin multiplicity should be same or $\Delta S = 0$

A is not allowed transition as $\Delta S \neq 0$

(b) ΔL = +/-1 , 0 for allowed transition as $\Delta L \neq 0, \pm 1$

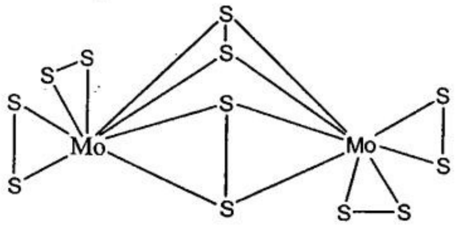
therefore E transition not allowed as $\Delta L \neq 0, \pm 1$

B, C, D are allowed .

27) a

$[Mo_2(S_2)_6]^{-2}$

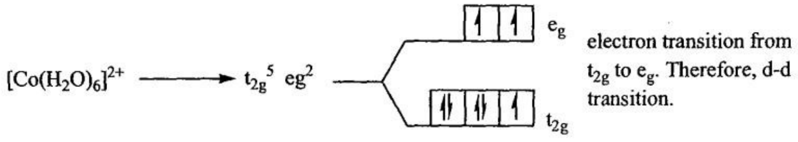
The structure of $[Mo_2(S_2)_6]^{-2}$ cluster is:

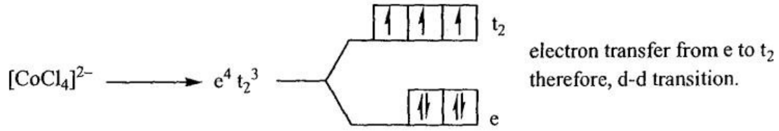


So, the bridging $S_q^{\$q}$, is two and co-ordination number of Mo is 8**.**

28) c

$[Co(H_2O)_6]^{+2} \rightarrow \mathbf{t^5_{2g}\ \ e^2_g}$


$[Co(H_2O)_6]^{2+}$
$t_{2g}^5\ eg^2$
e_g
t_{2g}
electron transition from t_{2g} to e_g. Therefore, d-d transition.

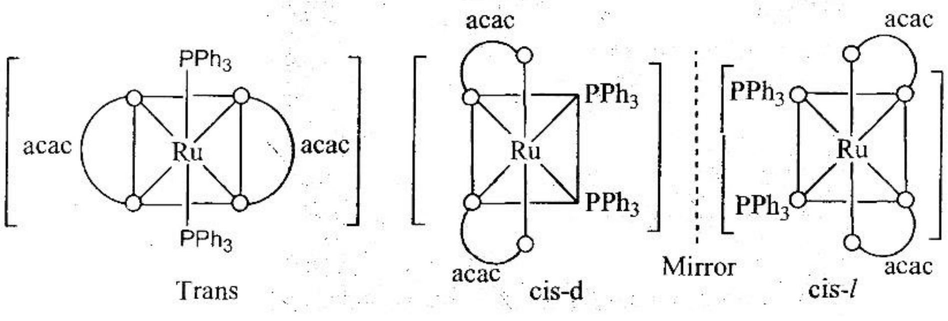

$[CoCl_4]^{2-}$
$e^4\ t_2^3$
t_2
e
electron transfer from e to t_2 therefore, d-d transition.

In this electron transition from $\mathbf{t^5_{2g} \rightarrow e^2_g}$ **,** therefore d-d transition.

$\mathbf{[CoCl_4]^{-2} \ \ \rightarrow t^5_{2g}\ \ e^2_g}$

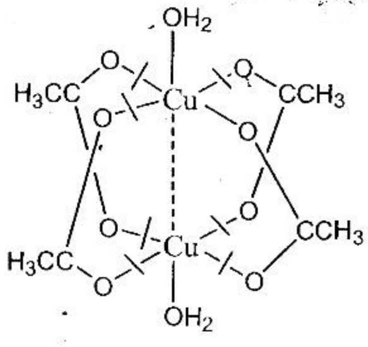
Electron transfer from e to t_2 , therefore d-d transition.

29) b



Total isomers = geometrical isomer + ½(optical isomer)
Geometrical isomer = 2 isomers (trans form + cis form)
Optical isomer = 2 isomers (d –cis-form + l-cis form)
Total isomers= 3

30) a



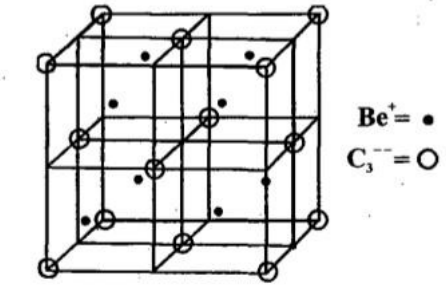
10 Cu–O bonds

31) c

Electric dipole allowed transition in d^2
For electronic transition selection rule, spin multiplicity ΔS=0; Δl= ±1, ΔJ = 0, ±1
^{3}**F**→ ^{3}**D** is allowed transition because ΔS=0, Δl = -1

32) d

In Be_2C_3 , Be^+ = In tetrahedral voids



C_3^{-2} = In FCC arrangement (Lattice point at corner + at each face centre)
Therefore, coordination number of Be^+ = 4
And coordination number of C_3^{-2} = 8

33) a

In trigonal bipyramidal complexes, the two ligands lie on z-axis and the three in xy plane somewhere in between the axes. In xy plane, there are four electrons and on z-axis there is only one electron in d_{t^u} orbital
Electronic Configuration, $d^{q}_{vt} = d^{q}_{wt} < d^{q}_{vw}$, $=d^{q}_{v^u \$ w^u} < d^{q}_{t^u}$

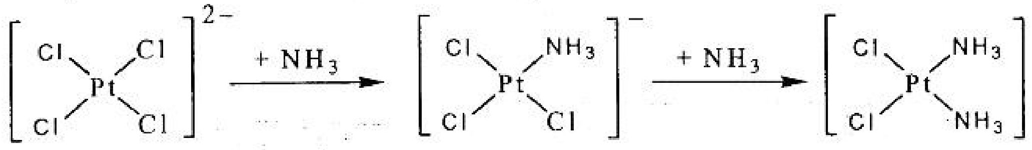
34) a

Co_3O_4 is a normal spinel. In normal spinel the Co^{+2} ions occupy tetrahedral voids and Co^{+3} ions occupy octahedral voids. Therefore, spinel structure of Co_3O_4 is
$(Co^{+2})_t (2CO^{+3})_o O_4$

35) a

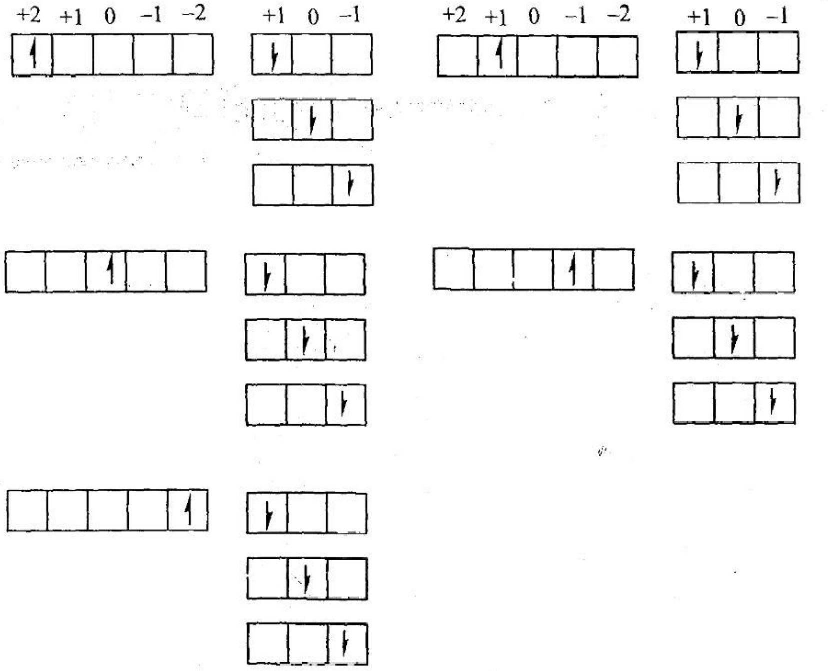
Trans effect of Cl^- > NH_3
Anti-tumour agent is cis-$[Pt(NH_3)_2CI]$

The precursor of this complex is $[PtCl_4]^{-2}$



36) b

Explanation



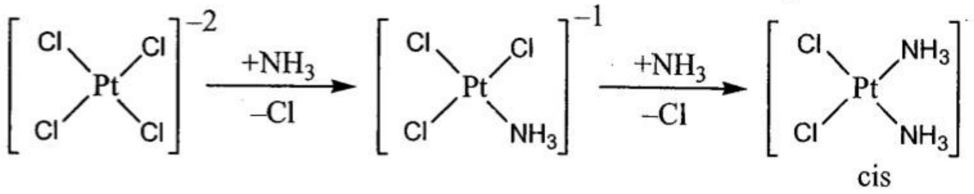
37) a

The rate of water exchange in $[Cu(H_2O)_6]$ is fastest due to Jahn-Teller distortion. For other three complexes of 3d-series dipositive metal cation, the rate of water exchange decreases with increase in effective nuclear charge and decrease in size.

Correct order: (i)> (ii)> (iii)> (iv)

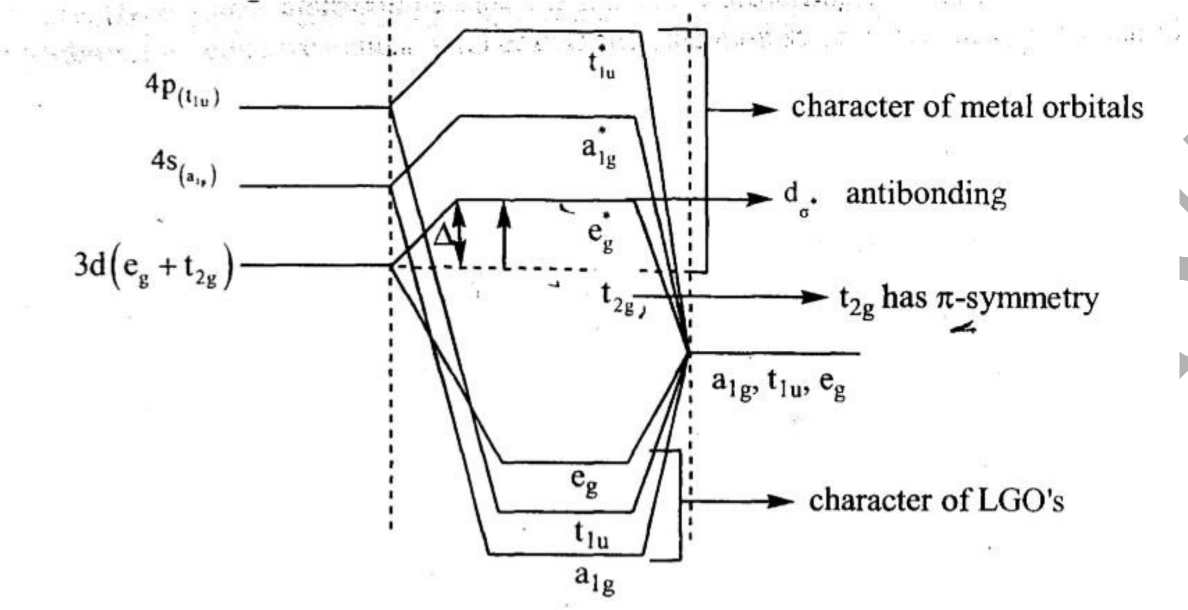
38) a

Trans effect Cl^- has larger trans effect than NH_3



39) b

The electronic transition responsible for the colour of the transition metal ions is **$d_\pi \rightarrow d_\sigma^*$** which is in according to LFT.



40) c

The mulliken symbols for the spectroscopic states arising from free ion term F are **$T_{1g} + T_{2g} + A_{2g}$**

41) c

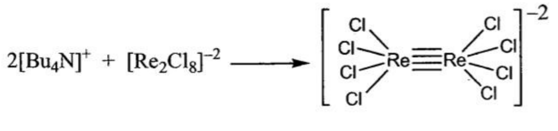
Co(II), Zn(II) and Be(II) form tetrahedral complexes with **Cl^-** or **OH^-.**
Be(II) has no d-orbitals, therefore it form tetrahedral complexes.
Co(II) and Zn(II) form tetrahedral complexes with halides and OH^-.

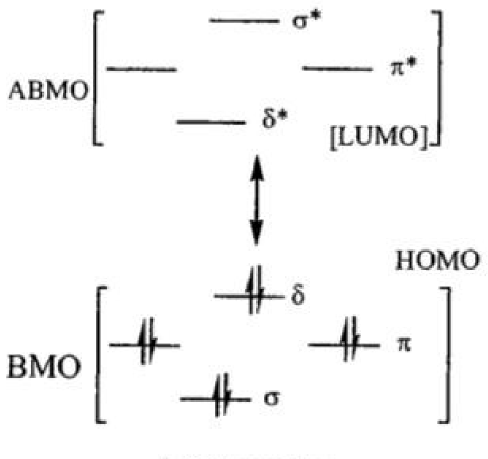
42) a

$[CoCl_4]^{2-}$ +6H_2O(blue) ↔ $[Co(H_2O)_6]^{2+}$+4Cl^-
(blue, tetrahedral) (Light pink, octahedral)

43) b

$[Bu_4N]_2 Re_2 Cl_8$





δ–δ* transition

44) d

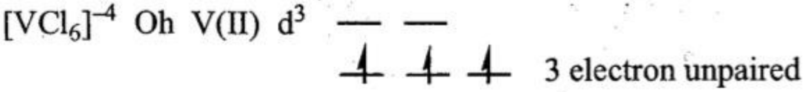
Among the given ligand CO is most **π** - acid ligand. Between C_2H_4 and C_2F_4 , C_2F_4 has more tendency to behave as л-acid ligand due to more electronegative F atoms which holds electron density towards F atoms and alkene behaves as a better **π** -accepting position from metal. NEt_3 has very little behaviour towards л-back bonding. Thus, the order is

$NEt_3 < C_2H_4 < C_2F_4 < CO$

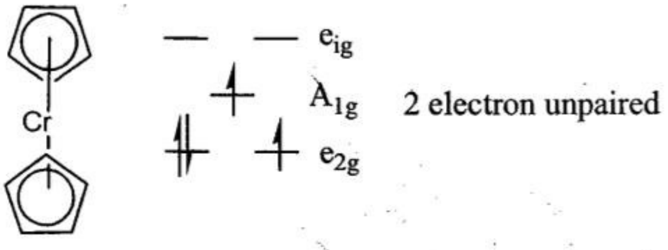
45) a

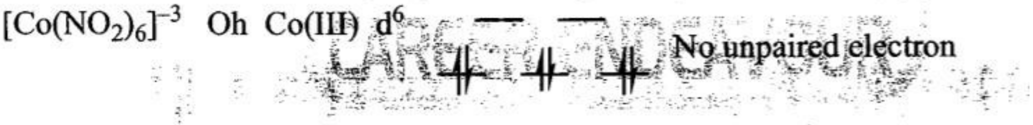
VCl_6^{4-}

Oh = V^{+2} = d^3



(η^5-C_5H_5)$_2$ Cr





$[Co(NO_2)_6]^{3-}$

Oh = Co^3 = d^6 → no unpaired electron.

[Ni(EDTA)]$^{2-}$

Ni^{+2} = d^8 → square planar → no unpaired electron.

More unpaired electron in **VCl_6^{4-}**

So, it contain highest magnetic moment.

$\mu = \sqrt{3(3+2)} = \sqrt{15}$ B.M

46) b

Intensity of C $^{4}\mathbf{A}_{2g}\rightarrow{}^{2}\mathbf{E}_{g}$ is lowest, since it is spin forbidden.

47) a

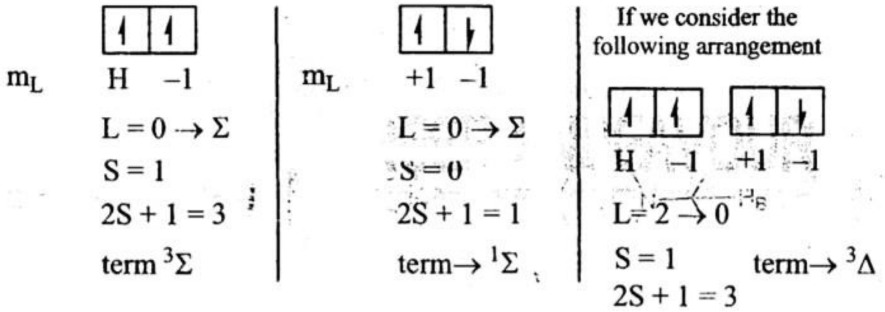
As strong field ligand have high crystal field stabilisation energy, according to spec trochemical series of ligand, the given ligand in order $Br^{-} < Cl^{-} < NCS^{-}$
Thus, Δ_t of given complexes follow the order: $\mathbf{[Co(NCS_4)]^{2-} > [Co(Cl_4)]^{2-} > [Co(Br_4)]^{2-}}$

48) a

$Co^{2+}\rightarrow t^{5}_{2g}\ e^{2}_{g}\rightarrow \mu = 3.89BM$
$Cr^{2+}\rightarrow t^{4}_{2g}\ e^{2}_{g}\rightarrow \mu = 4.9BM$
$Mn^{2+}\rightarrow t^{3}_{2g}\ e^{1}_{g}\rightarrow \mu = 4.9$ BM
$Fe^{2+}\rightarrow t^{4}_{2g}\ e^{2}_{g}\rightarrow \mu = 4.9BM$

49) d

For two non-equivalent π-electrons $[\pi^1, \pi^1]$



$^3\phi$ is not possible.

50) c

Order of ligand is spectro chemical series
$SCN^{-} < Cl^{-} < F^{-} < CN^{-}$
From above it is clear that CN^{-} will produce highest energy difference, followed by F^{-}, Cl^{-}, SCN^{-}. As colour of complex is complementary colour of absorbed light.
Thus $\mathbf{[Co(CN_4)]^{2-}}$ absorbs orange colour radiation which complementary colour is blue therefore colour of $\mathbf{[Co(CN_4)]^{2-}}$ is blue.

The other combination according to energy are mismatched. Hence, only option (c) is correct.

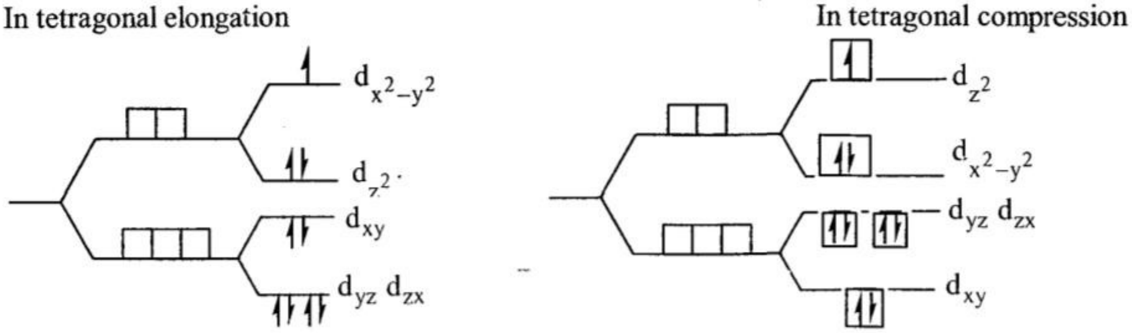
51) d

$Mn^{2+}\rightarrow 3d^{5}\rightarrow \mathbf{t^{3}_{2g}\ e^{2}_{g}}$ (high spin octahedral)
CFSE in Oh field=(-0.4×3 +0.6×2) =0

$Cr^{+3}\rightarrow 3d^{3}\rightarrow \mathbf{t^{3}_{2g}\ e^{0}_{g}}$ (octahedral)

CFSE in octahedral field = $-0.4\text{x}3\Delta_0 = -(0.4\text{x}3)\ \Delta o = -1.2\Delta o$

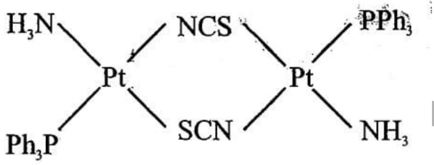
52) b



53) c

Pt-S→ dπ-dπ bonding in weaker than that of Pt-P bonding. When Pt-S and Pt-P bond are trans to each other then Pt-S become weaker therefore in such a situation SCN ligand tends to form bonding through M atoms of ligand as M do not do not form dπ-pπ bonding. Hence, the most probable structure will be

(c)



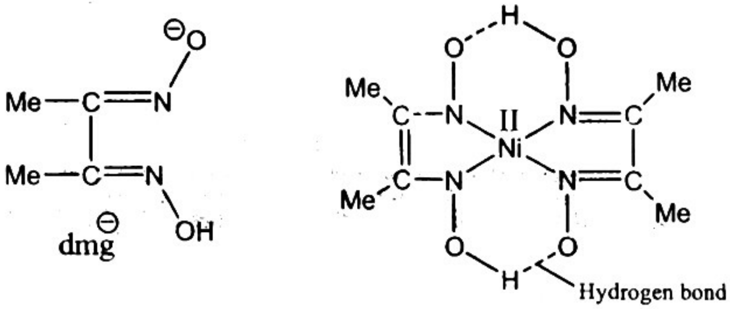
54) a

Ni^{2+} is tested by dmg

Ni^{2+} + 2dmg → $[Ni(dmg)_2]$ (Tschygaeff test)

Red

The structure of complex is



Therefore

Ni-N bonds = 4

Ni-O = 0

Hydrogen bonds = 2

55) a

$NiBr_2$ reacts with (Et)(Ph_2)P at -78°C in CS_2 gives red copound 'A' which on standing at room temperature turns green to give B.

Measured magnetic moments of 'A' is 0.0 BM (no unpaired electrons)
and 'B' is 3.2 BM (two unpaired electrons + orbital contribution)

For A geometry of Ni^{2+} = $3d^8\,4s^0$ = hybridisation = dsp^2 (square planar)

For B geometry of Ni^{2+} = $3d^8\,4s^0$ = $\mathbf{t^6_{2g}\ e^2_g}$ = two unpaired electrons, hybridisation = sp^3 (Tetrahedral)

56) a

In $\mathbf{[AgL_4]^{2+}}$ and $\mathbf{[AgL_6]^{2+}}$, Ag^{2+} has d^9 configuration, hence have unpaired electron. Hence paramagnetic.

$\mathbf{[AgL_4]^{3+}}$, Ag^{3+} has d^8 configuration and dsp^2 hybridization (square planar so pairing of electron). Hence, diamagnetic in nature

57) a

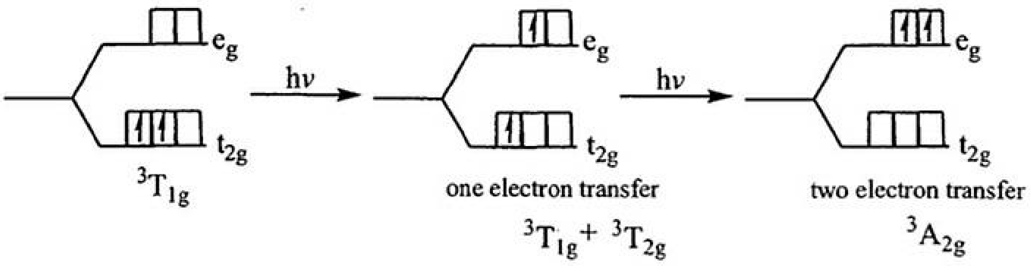
$\mathbf{[CoL_6]^{3+}}$ →red colour→ absorbs green radiations

$\mathbf{[CoL'_6]^{3+}}$ →green colour→ absorbs red radiations.

Energy of green radiations > energy of red radiations, Therefore, L will be stronger ligand than L'. Thus, L and L' are NH_3 and H_2O respectively.

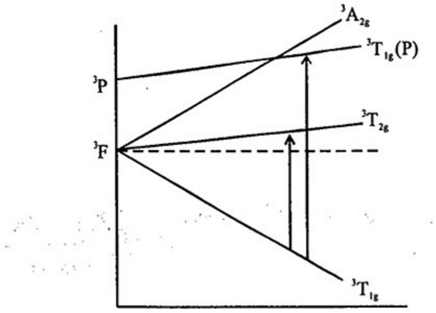
58) a

$[V(H_2O)_6]^{3+} \rightarrow V^{3+} \rightarrow 3d^2 \rightarrow t^2\, eg^o$



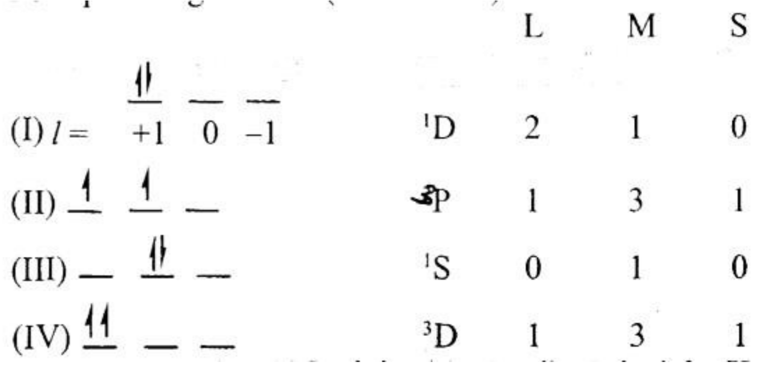
Two transition

$V_1 = {}^3T_{1g}\,(F) \rightarrow {}^3T_{2g}\,(F)$; $V_2 = {}^3T_{1g}\,(F) \rightarrow {}^3T_{1g}\,(P)$



59) d

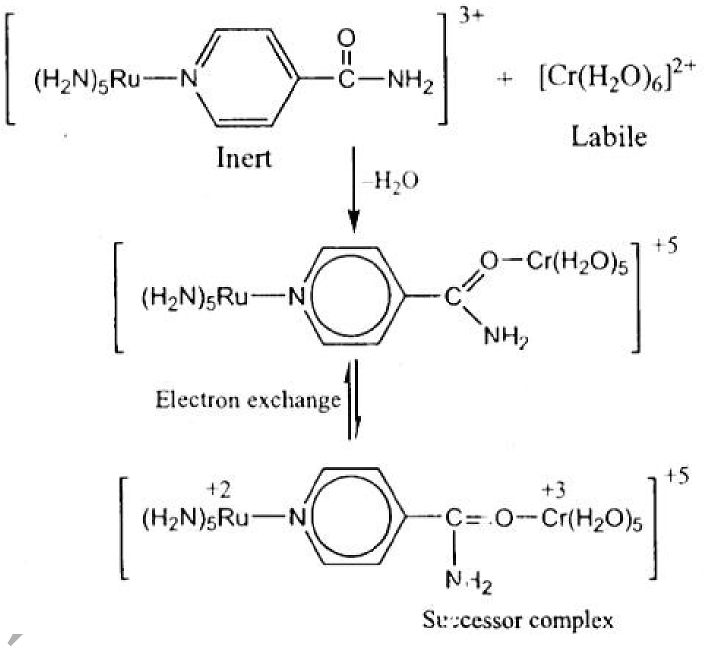
For np^2 configurations (microstates)



		L	M	S
(I) l = ↿⇂ (+1) __ (0) __ (−1)	^1D	2	1	0
(II) ↿ ↿ __	^3P	1	3	1
(III) __ ↿⇂ __	^1S	0	1	0
(IV) ↿↿ __ __	^3D	1	3	1

The configuration (IV) violets the Pauli's Principle, Hence term symbol ^3D is not possible.

60) a



In the successor complex inert ruthenium bridged to inert chromium.

61) a

(Phen) is an π-acceptor ligands hence there is mixing of donor and acceptor orbital having similar symmetry this leads to fast transfer of electron leading to enhance rate of reaction.

$[Fe(phen)_3]^{+3}$ $[Fe(phen)_3]^{+2}$

↓ ↓

$t^5_{2g}\ e^0_g$ $t^6_{2g}\ e^0_g$

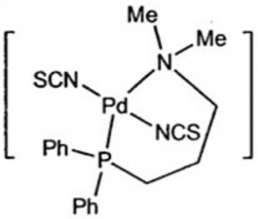
$\pi^{*5}\sigma^{*0}$ $\pi^{*6}e^0_g$

Electron transfer takes place from π^{*6} (Fe^{+2})→ π^{*5} (Fe^{+3})

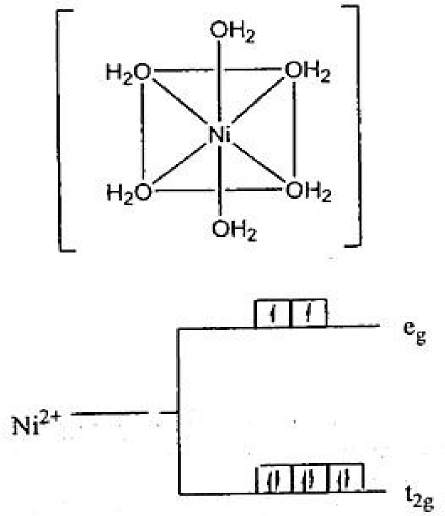
Correct answer is (a)

62) a

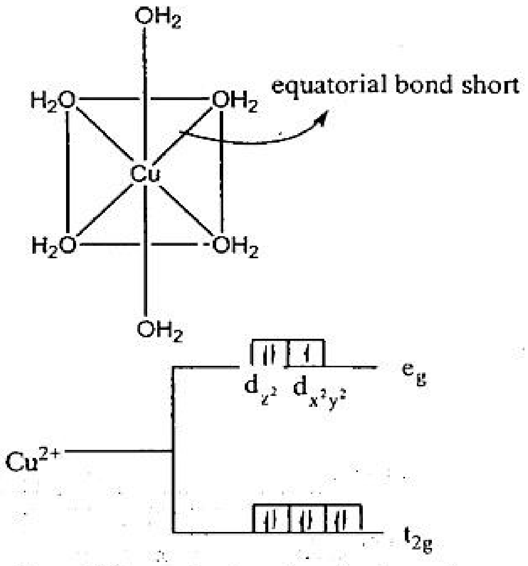
s and p both form π -bonding with complex and π-bonding capacity of sulphur is greater than phosphorus due to smaller size of d-orbital of sulphur. Hence, in presence of sulphur trans to phosphorus donor atom phosphorus-metal bond will be weak hence they do not lie trans to each other in the complex. As nitrogen does not involment in π -bonding with complex hence when nitrogen atom is trans to phosphorus, phosphorus become able to form efficient π -bond with metal hence become stable thats why P and N are trans to each other



63) c

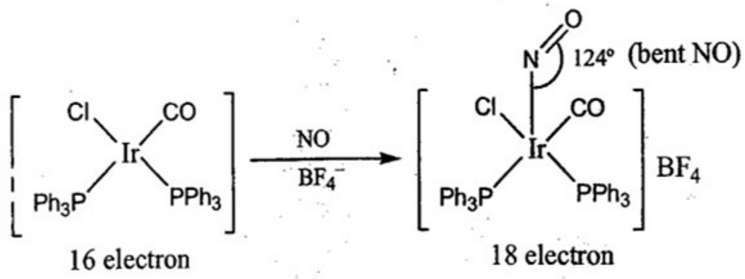


Symmetrical electronic environment so all bond length same



There is large electron density at z-axis So, on z-axis increases

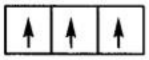
64) a



Terminal NO=1672 cm^{1}
Bridging NO=1505 cm

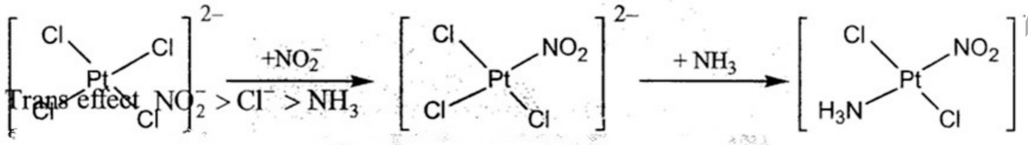
65) d

N=1s 2s 2p
L= +1 0 -1



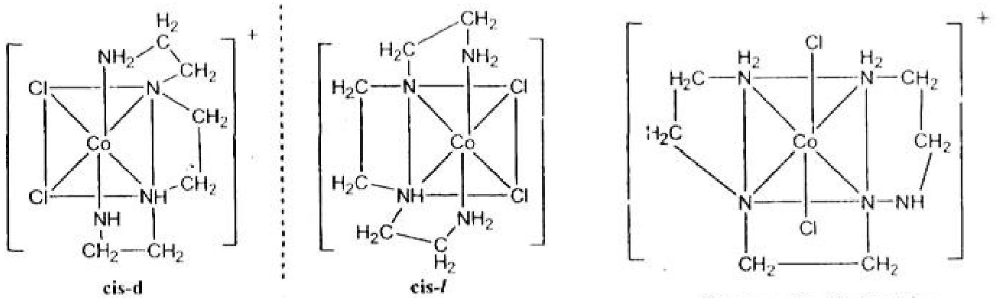
S= 1/2+1/2+1/2=3/2
L=+1+0-1=0

66) a



Trans effect $NO_2^- > Cl^- > NH_3$

67) c



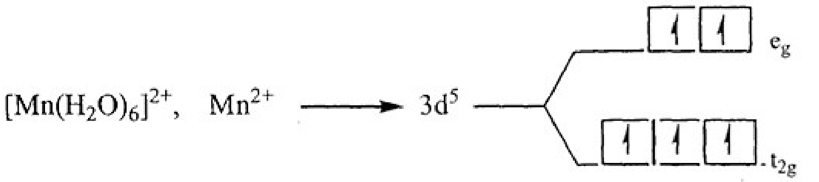
cis-d

cis-*l*

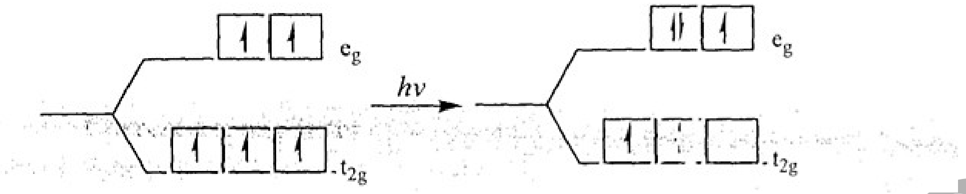
Trans optically inactive

Total isomers = geometrical isomer + ½(optical isomer)
Geometrical isomer = 2 isomers (trans form + cis form)
Optical isomer = 2 isomers (d –cis-form + l-cis form)
Total isomers= 3

68) a
Explanation



Ground state term for d^5 is ^6S which transform into $^6A_{1g}$ in octahedral field.



There is spin change during electron transition. Therefore, transition is spin disallowed

69) a

$[CoCl(NH_3)_5]^{+2} + OH^- \rightarrow [Co(NH_3)_4(NH_2)Cl]^{+1} + H_2O$

$[Co(NH_3)_4(NH_2)Cl]^{+1} \rightarrow [Co(NH_3)_4(NH_2)]^{+2} + Cl^{-1}$

$[Co(NH_3)_4(NH_2)]^{+2} + OH^- \rightarrow [Co(NH_3)_5OH]^{+2}$

Base hydrolysis of **$[CoCl(NH_3)_5]^{+2}$** depends on the concentration of both **$[CoCl(NH_3)_5]^{+2}$** and base. In this reaction OH^- abstract proton from coordinated NH_3.
The base hydrolysis of **$[Co(CN)]^{-3}$** is independent of base because it has no ionizable proton.

70) c

$[Ne]\ 2p^1\ 3p^1$
$2s+1=3;\quad 2s=2;\quad s=1$

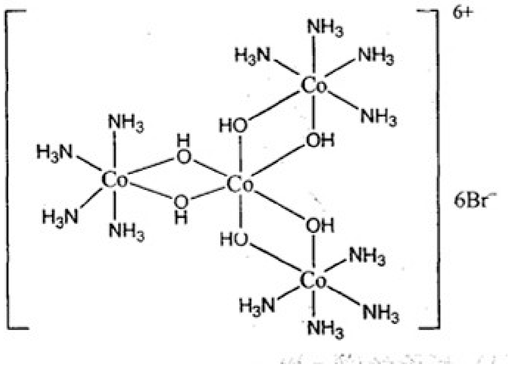
For, D, L=2
$J=|L+s|.....|L-s|=|2+1|...|2-1|= 3,2,1$
Levels for ^3D are **$^3D_3$, $^3D_2$, $^3D_1$**

71) a

$[MnF_6]^{-3}$, $Mn^{+3} \rightarrow 3d^4 \rightarrow t_{2g}^3 e_g^1$
(HS)
$\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.9$
S =2 → $2s+1 = 2\times2+1=5$
L=2→D
Ground state term symbol ^3D

72) a

It is first inorganic optically active compound discovered by Werner.



Number of Co-O bonds = 12
Number of Co-N bonds 12

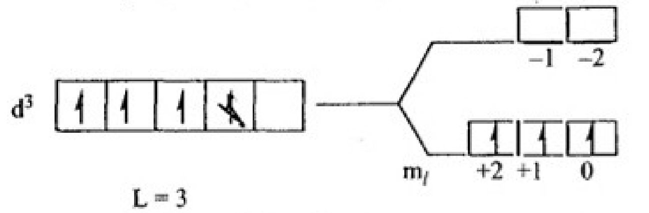
73) a

$[CrCl_6]^{-3}$

$Cr^{3+} \rightarrow 3d^3$

$\mu_s = \sqrt{n(n+2)} = \sqrt{3(3+2)} = 3.87$

$\mu_{L+S} = \sqrt{n(n+2)+l(l+1)}$ BM

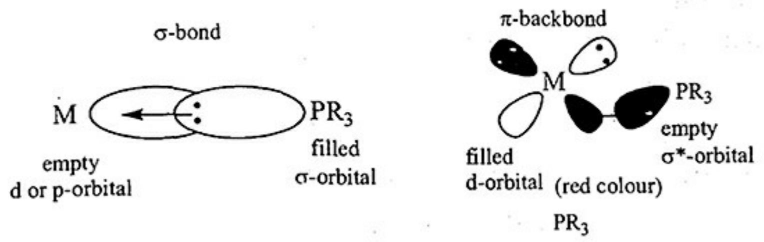


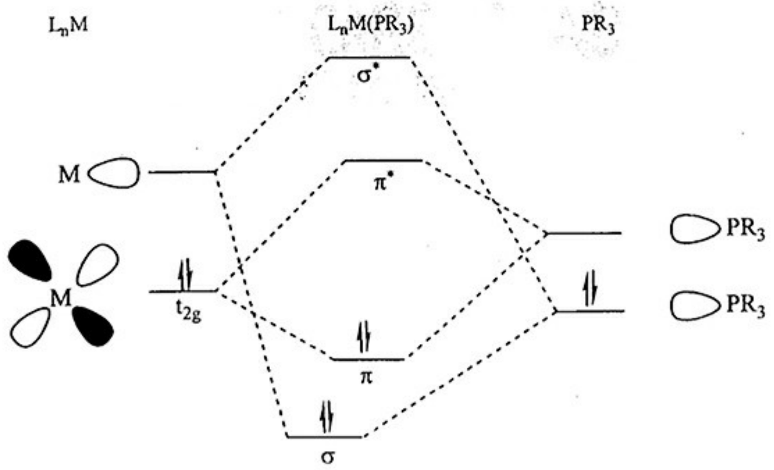
$$\mu_{L+S} = \sqrt{3(3+2)+3(3+1)} = \sqrt{15+12} = \sqrt{27} = 5.20 \text{ B.M.}$$

$\mu_{L+S} = \sqrt{n(n+2)+l(l+1)} = \sqrt{3(3+2)+3(3+1)} = \sqrt{15+12} = \sqrt{27}$ = 5.20 BM

74) a

The bonding in phosphine ligands, like that of carbonyls having two components. The primary component is sigma donation of the phosphine lone pain to on empty orbital on the metal. The second component is back donation from filled metal orbital to an empty orbital on the phosphine ligand. This empty phosphorous orbital has been described as being either a d-orbital or an antibonding sigma orbital (ϭ*).





So, in transition metal phosphine (M-PR_3) complexes, the back bonding involves donation of electrons from **$M(t_{2g}) \rightarrow PR_3(\sigma^*)$**

75) b

For allowed transition : a)Spin multiplicity should be same or $\Delta S = 0$

Option c and d (incorrect) as $\Delta S \neq 0$

b) $\Delta L = \pm 1$, for allowed transition

$$3S \rightarrow 3P$$
$$\Delta S = 3-3=0$$
$$\Delta L= 1-0= 1$$

76) d

$ns^1\ np^1$

$L=1\ \equiv P$

$S=1$ hence, $2S+1=3$

For J value, if orbital is less than half filled than

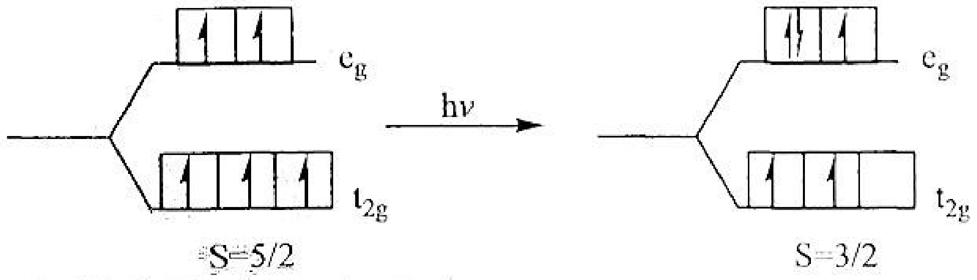
$J=|L-S|=|1-1|=0$

Hence, **$^3P_0$**

77) a

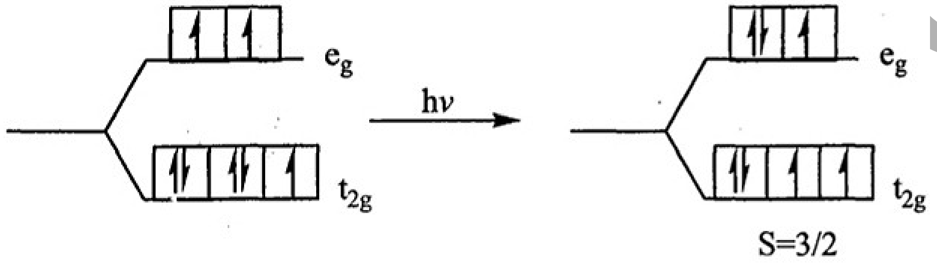
Fe(II) protoporphyrin → **$\pi \rightarrow \pi^*$** transition

$[Mn(H_2O)_6]Cl_2 \rightarrow Mn^{+2} \rightarrow d^5$ (high spin) spin forbidden (d-d) transition.



ΔS=1. Hence, not allowed.

$[Co(H_2O)_6]Cl_2 \rightarrow Co^{+2} \rightarrow d^7$ (high spin) (d-d)



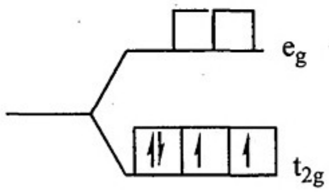
ΔS= 0. hence allowed

78) c

$K_4[Cr(CN)_6] = Cr^{+2} \rightarrow d^4$ (low spin)

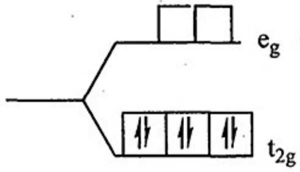
For a compound to show John Teller Distortion e_g or t_{2g} set should be electronically degenerate.

(1) $Cr^{+2} \rightarrow d^4$ (low spin)



Electronically degenerate hence show John Teller Distortion.

(2) $K_4[Fe(CN)_6] = Fe^{+2}$ (low spin) = d^6 (low spin)

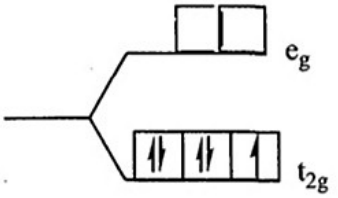


Electronically non-degenerate hence, no Jahn-Teller distrotion

(3) $K_3[Co(CN)_6] = Co^{+3} \rightarrow d^6$ (low spin)

Same as above hence, no Jahn-Teller Distrotion.

(4) $K_4[Mn(CN)_6]$ = Mn^{+2} (low spin)

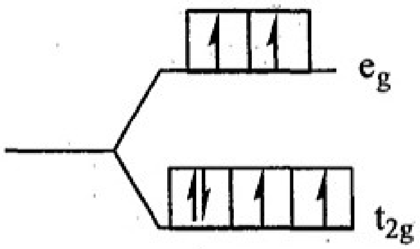


electronically degenerate

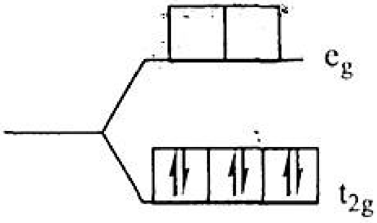
Hence, complex will show Jahn-Teller Distortion.

79) a

$[Fe(Phen)_2(NCS)_2]$
$Fe^{+2} = d^6$ complex
At high temperature high spin and at low temperature low spin behaviour at 250 K



CFSE = 1.6 Δ_0 +1.2 Δ_0 =0.44,
$\mu = \sqrt{n(n+2)} = \sqrt{4(4+2)}$ = 4.90 at 150 K



CFSE -0.4 x 6 Δ_0 = -2.4Δ
μ =0

80) a

Taking the valence shell configuration
Be $2s^1\ 3s^1$
s=1/2+1/2 =1
Multiplicity =2S+1= 2x1+1=**3**
L= 0+0= 0 , **S term**
J= (L+S) = (0+1) = 1
Hence, terms is $^3S_1$

81) a

$[CrO_4]^{2-} < [MnO_4]^{2-} < [FeO_4]^{2-}$

All have +6 oxidation state but due to smaller size on going from Cr to Fe, Fe has very high charge density. Hence, it has very high tendency to accept electron. Hence, strongest oxidising agent.

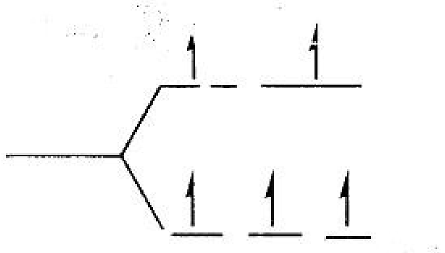
82) c

	Number of unpaired electrons
(A) **$[CoF_6]^{3-}$** $\rightarrow d^6$ (high spin) = $\mathbf{t^4_{2g}\ e^2_g}$	**4**
(B) **$[IrCl_6]^{3-}$** $\rightarrow d^6$ (low spin) = $\mathbf{t^6_{2g}\ e^0_g}$	**0**
(C) **$[Fe(H_2O)_6]^{2+}$** $\rightarrow d^6$ (high spin) = $\mathbf{t^4_{2g}\ e^2_g}$	**4**

Since, A and C has same number of unpaired electron. Hence, they have same magnetic moment. As A and Care 3d-block metal with weak ligand. Hence, they are high spin while Ir being 5d-metal is low spin. Because 5d has greater splitting power than 3d.

83) a

$[Mn(H_2O)_6]^{2+} = d^6$ (HS)



As all the levels are electronically non-degenerate. Hence, No Jahn-Teller distortion. Therefore, all the Mn-O bond length will be equal.

84) a

$[Fe(phen)_3]^{2+} \rightarrow [Fe(phen)_3]^{3+} + e^-$
(Red) (Blue)

In presence of oxidising agent like $K_2Cr_2O_7$, $[Fe(phen)_3]^{2+}$ changes it colours from red to blue hence, they are used in redox titration.

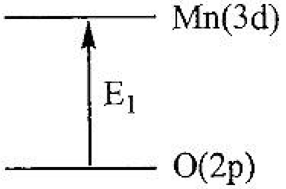
85) a

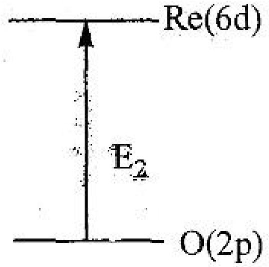
The stability (formation constant for complexation of cryptate complex depends upon)
(1) size of cavity
(2) size of metal cation

cryptand	suitable cation
crypt – 211	Li^+
crypt – 221	Na^+
crypt – 222	K^+

Hence, K^+ ion will form most stable complex with cryptand-222.

86) c





$E_2 > E_1$ hence, energy required for transfer of electron from oxygen to Re falls in UV region. Hence, **$[ReO_4]^-$** colourless while in **$[MnO_4]^-$** due to less energy difference it falls in visible region. Hence, **$[MnO_4]^-$** coloured. Also as both Mn and Fe have +7 oxidation state i.e. they have no d-electron hence, no d-d transition and colour arises due to LMCT.

87) a

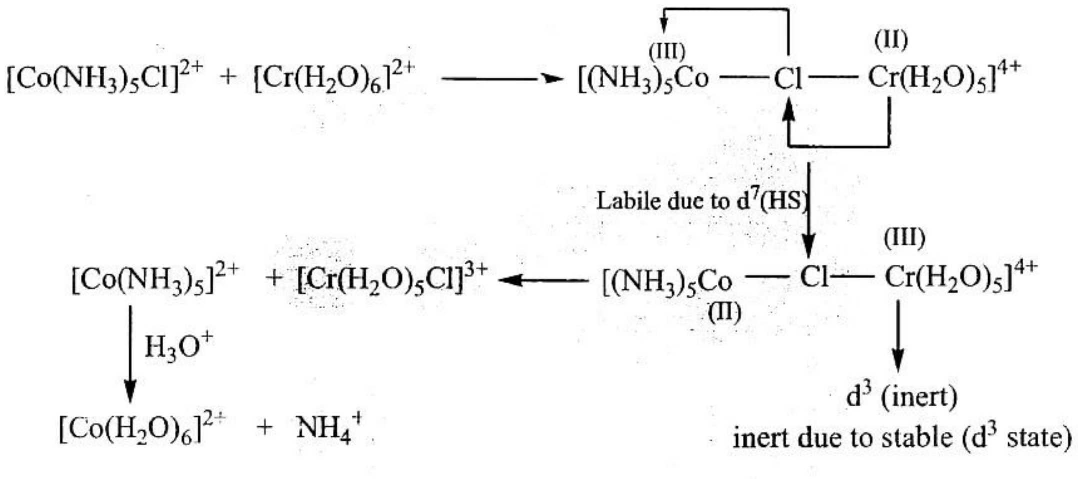
$[Co(CN)_5Cl]^{3-} + OH^- \rightarrow [Co(CN)_5(OH)]^{3-} + Cl^-$

The reaction proceed through dissociative pathway and rate is dependent only concentration of substrates. As substate do not have acidic hydrogen. Hence, it does not undergo S_N 1CB mechanism.

$[Co(CN)_5Cl]^{3-} \underset{\text{(slow)}}{\rightarrow} [Co(CN)_5]^{2-} + OH^- \rightarrow [Co(CN)_5OH]^{3-}$

88) a

Explanation

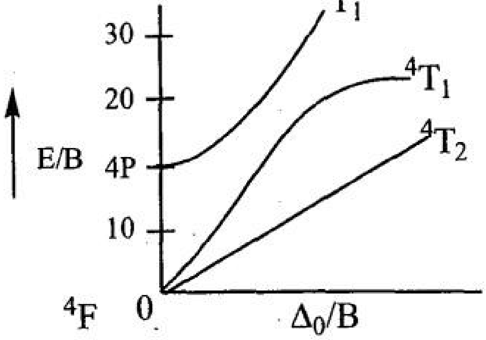

[Co(NH3)5Cl]2+ + [Cr(H2O)6]2+
[(NH3)5Co — Cl — Cr(H2O)5]4+
(III)
(II)
Labile due to d7(HS)
[Co(NH3)5]2+ + [Cr(H2O)5Cl]3+
[(NH3)5Co — Cl— Cr(H2O)5]4+
(II)
(III)
H3O+
[Co(H2O)6]2+ + NH4+
d3 (inert)
inert due to stable (d3 state)

89) c

Tanabe-Sugano are useful in interpretation of spectra of both **high spin and low spin** complexes of d^2-d^8 metal cation.

In Tanabe-Sugano, the energy of excited sate (expressed as E/B) are plotted against ligand field strength (expressed as (Δ_0 /B).

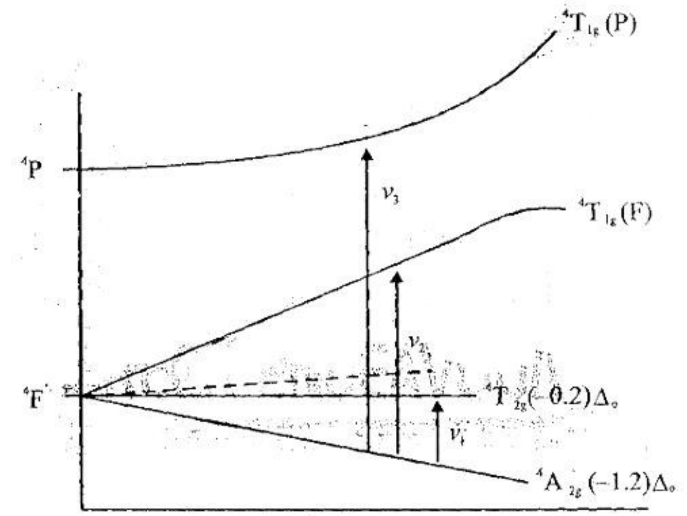
Zero energy is taken for the lowest term and also two form of same symmetry never cross each other and they bent for apart from each other due to repulsion.



90) b

$[CrF_6]^{-3} = d^3$

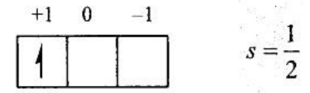
Orgel diagram for d^3.



ground state= ^4F
First excited state = ^4P
$^4A_2g \rightarrow {}^4T_2g$ (Δ_0)

v_1 = 14900 cm^{-1} ; v_2 = 22700 cm^{-1} ; v_3 = 34400 cm^{-1}
Since, ^4T_1g (P) and ^4T_1g (F) have no fix energy therefore, they will not provide accurate value of Δ_0.
Thus, energy difference between $^4A_2g \rightarrow {}^4T_2g$ 14900 cm $^{-1}$ will be correspond to Δ_0

91) b
For [$1s^22s2p^6$ $3p^1$]



$2s+1=2\times\frac{i}{q}+1=2$
J=|l+s|..... |l-s|
=|1+½|.....|1-½|
= 3/2 1/2
Term symbol $^2P_{3/2}$ $^2P_{1/2}$

92) b
$^3F \rightarrow {}^3D$
Since, for allowed transition (atomic), $\Delta S=0$, $\Delta L=0,\pm1$
In option a and c spin multiplicity is not same therefore incorrect
In option d , $\Delta L=2$ therefore incorrect.

93) d
[$Ni^{II}L_6$] $^{n+ \text{ or } n-}$ has shows absorption bands at 8500, 15400, and 26000 cm^{-1}
[Ni^{II} L'_6] $^{n+ \text{ or } n-}$ at 10750, 17500 and 28200 cm^{-1}

as for first complex absorptions bands are at low energy i.e. it has weak splitting therefore, it has weak ligand and for II complex high energy absorption bands corresponds to strong ligand.Thus, L is weak and L' is strong ligand.

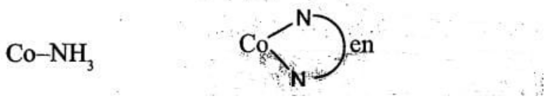
94) b

Number of microstate in **^{3}F** is calculated as (2S + 1) (2L+1)
For F, L=3.
Hence, (3) (2x3+1) =21

95) b

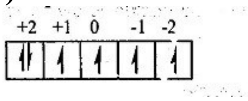
Chelate effect is predominately due to entropy change

$$[Co(NH_3)_6]^{3+} + 3en \rightleftharpoons [Co(en)_3]^{3+} + 6NH_3$$



ΔH nearly same but entropy change is more.

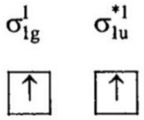
96) b



D^6 =
L= ∑M$_L$ = 5-3 = 2 = D
S=2 , 2S+1=5
Hence, lowest energy form = ^{5}D

97) d

H$_2$ (excited state)



L = 0 = Σ
S=1/2+1/2= 1 , 2s+1=3
gxu=u = $^3\sum_u$
For half filled.

98) c

[Cr(bipyridyl)$_3$]$^{+3}$→ d^3 = 4F (ground state term)
As phosphorescence is spin-forbidden transition and also occurs when electron comes from excited to ground state. Hence, transition **$^4A_{2g} \leftarrow {}^2E_g$** is responsible for the phosphorescence**.**

99) c

For orbital contribution the set should be unsymmetrically filled
[Cu(H$_2$O)$_6$]$^{+2}$→ **t_{2g}^6 e_g^3** →No contribution
[Ni(H$_2$O)$_6$]$^{+2}$→ **t_{2g}^6 e_g^2** →No contribution

$[Co(H_2O)_6]^{+2} \rightarrow \mathbf{t^5_{2g}\ e^2_g} \rightarrow$ Orbital contribution
$[Cr(H_2O)_6]^{+2} \rightarrow \mathbf{t^3_{2g}\ e^1_g} \rightarrow$ No contribution

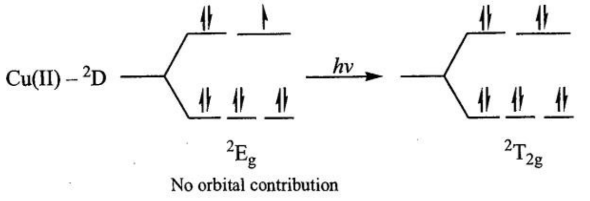
100) d

In $KMnO_4$ all the electrons are paired. However, its paramagnetic susceptibility of the order of 10^{-6} cm^3 mol^{-1} is due to the temperature independent paramagnetism.

101) a

The complexes having T ground state have orbital contribution to magnetic moment however for complex having A or E ground state some time μ_{eff} is slightly greater than μ_{spin} is due to mixing of first excited state T (having same spin multiplicity to ground state) mixes with A or E due to spin coupling and there is calculated by

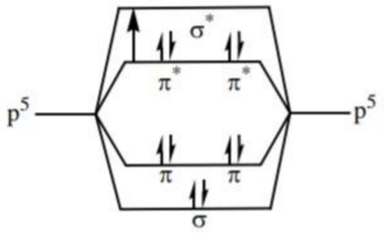
$$\mu_{eff} = \mu_s \left(1 - \frac{\lambda\alpha}{\Delta}\right)$$



Hence, higher value of $\mu_{eff} = \mu_s \left(1 - \frac{\lambda\alpha}{\Delta}\right)$

102) a

In halogen molecules, the **π*→ σ***transitions are responsible for their colours as evident from the following figure



103) a

The-donor ligands such as Cl^-, Br^-, I^-, N-bonded NCS^- etc stabilize the TBP intermediate and favour the stereochemical change. The trans-forms tendency to isomerise in the order

$A = NO_2^- < Cl^- < NCS^- < OH$

104) d

According to Nephelauxetic series

$F^- > H_2O > NH_3 >$ en $> NCS^- > Cl$ CN $^- > Br^-$

The highest value of   is for F^-

105) **a**

The $^{2}E_{g} \leftarrow {}^{4}A_{2g}$ transition in the electronic spectrum of **$[Cr(NH_3)_6]^{+3}$** occurs nearly at 650 nm.

106) **c**

$[Cr(NH_3)_6]^{+3}$

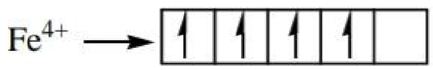
$Ce^{+4} \rightarrow 4f^{0} \rightarrow$ No f-f Transition

No unpaired electrons.

It is diamagnetic and its colour is due to LMCT. Its C.N. = 10

107) **c**

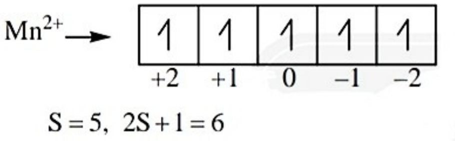
$[FeO_4]^{-4}$ → Jahn-Teller distorted away from the ideal tetrahedral towards a flatterred structure



it is paramagnetic due to unpaired electron D_{2d} symmetry

108) **b**

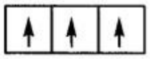
$[Mn(H_2O_6)]^{+2} \rightarrow H_2O$ is a weak ligand, No pairing occurs.



S=5/2 , 2S+1=6

L=0→ S Term

Ground state term → ^{6}S



Cr^{+3} =

L= 3→F Term

S= 3/2 ; 2S+1=2x3/2+1=4

Ground state term→ ^{4}F

$Cu^{+2} = d^{9}$

L= $\sum M_L$ = 2 →D

S=1/2 , 2S+1=2

Ground state term → ^{2}D

109) **b**

$[CoCl(NH_3)_5]^{+2} + OH^{-} \rightarrow [Co(NH_3)_4(NH_2)Cl]^{+1} + H_2O$

$[Co(NH_3)_4(NH_2)Cl]^{+1} \xrightarrow{\text{‡ˆ‰Š ‡‹Œ•}} [Co(NH_3)_4(NH_2)]^{+2} + Cl^{-1}$

$[Co(NH_3)_4(NH_2)]^{+2} + OH^{-} \rightarrow [Co(NH_3)_5OH]^{+2}$

110) **b**

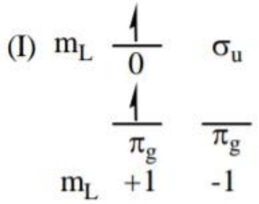
( ) $\sqrt{k(11)K=2(2f)}=$ $\sqrt{5\times4\times10' \times2\times10'}$ $\Rightarrow\times 2.0\times10^{k} = 2.0\times10''$

111) **a**

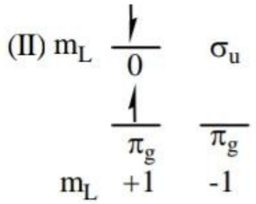
Fischer carbene carbon is electrophilic in nature due to strong π- acceptor ligands

112) a

The arrangements for **[1π_g]^1 [3σ_u]^1**configurations are



S= 1, 2S+1=3
L=1→ πTerm
Spectroscopic Term = $^3\pi$



L=1→ πTerm
S=0, 2S+1= 1
Spectroscopic Term → ^{1}S
Thus one of possible moleculer term symbol is $^1\pi$

113) a

In CdS, HgS and Bi**I_3** colour is due to LMCT as Cd^{+2} and Hg^{+2} has d^{10} configuration. Hence, no d-d transition. Also, no MLCT as ligand is not π -acceptor.

114) a

Change in CFSE on going for Oh to five coordinate intermediate for ions is as follows.
V^{+2} (d^3) = -2.00
Cr^{+3} (d^3) = -2.00
Ni^{+2} (d^8) = -2.00

115) a

NR → Dithiocarbamate
OR → Xanthate
O^- → Dithiocarbonate
SR → Thioxanthate

116) b

$$\mu_{eff} = \mu_s \left(1 - \frac{”\bullet}{–}\right)$$

$\Delta = \frac{i}{”}$ $\frac{i}{“qk}$ × $10^{\$—}$ $\frac{ij\ \check{s}›}{“qk}$ cm = cm^{-1}

For Cu^{+2} → Term is ^2D , hence, $\alpha = 2$, $\lambda = -625\ cm^{-1}$

$\mu_{eff} = 1.73\left(1 - \frac{\text{q×\$“qk)×“qk}}{\text{ij ›}}\right) = 1.73\left(1 + \frac{\text{q×“qk   ×“qk}}{\text{ij ›}}\right)$

$1.73\left(1 + \frac{\text{q×“qk   ×“qk}}{\text{ij ›}}\right) = 1.73\{1 + 0.078\} = 1.73\{1.078\} = 1.864$

$\mu_{eff} = 1.864$

117) a

As the strength of ligand increases energy for d-d transition increases.

Strength of ligand order is $F^- < ox^{-2} <$ en. Option A is correct .

All complex have same number of unpaired electron. Hence, all have same spin only magnetic moment. Option B is correct .

$[Cr(ox)_3]^{-3}$ and **$[Cr(en)_3]^{+3}$** will show optical isomer. As t_{2g} level is electronically non-degenerate. Hence, there will be no Jahn-Teller distortion. Option D is incorrect .

118) a

Thus, order for energy absorption is 675 (A) < 615 (B) < 565 (C)

Δ_0 increases as the ligand field strength increases $H_2O < NH_3 <$ en

Complementary colour of blue → Orange , green →Red, Violet → Yellow

Energy order for absorbed light is yellow > orange > red

Thus, A absorbs red hence it is green

B absorbs orange hence it is blue

C absorbs yellow hence it is violet

119) d

(A) **$[TiF_6]^{-3}$**

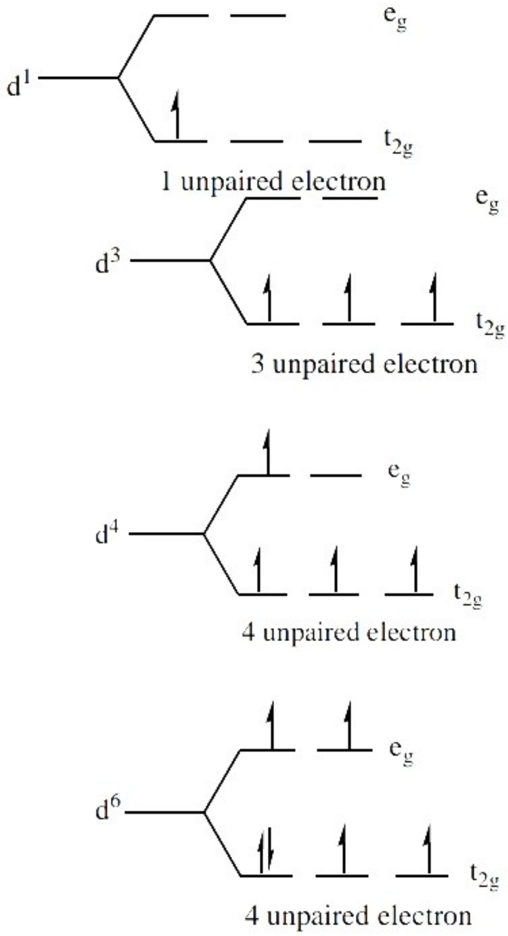
$Ti \Rightarrow 3d^2\ 4s^2$

$Ti^{+3} \Rightarrow 3d^1\ 4s^0$

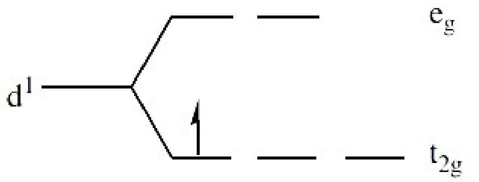
(B) **$[CrF_6]^{-3}$**

$Cr = 3d^5\ 4s^1$

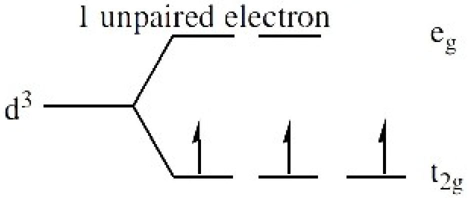
$Cr^{+3} = 3d^3\ 4s^0$



(C) **$[MnF_6]^{-3}$**
$Mn = 3d^5\ 4s^2$
$Mn^{+3} = 3d^4$

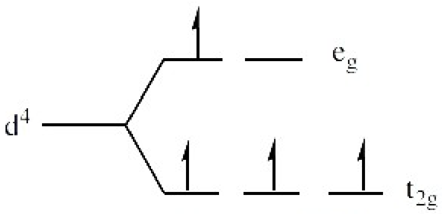


1 unpaired electron

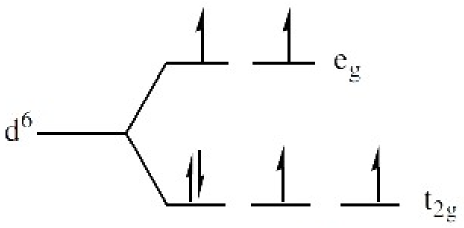


3 unpaired electron

(D) **$[CoF_6]^{-3}$**
$Co = 3d^7\ 4s^2$
$Co^{-3} = 3d^6\ 4s^0$



4 unpaired electron

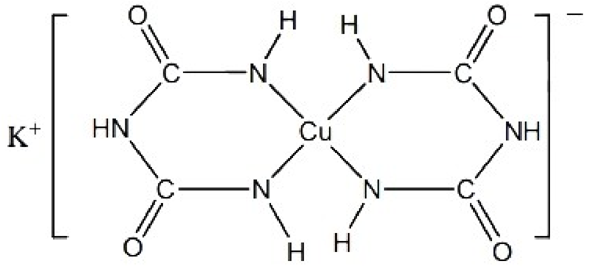


4 unpaired electron

Hence, $A < B < C \approx D$

120) **a**

$K_2CuF_6 = 3K^+\ [CuF_6]^{-3}$ oxidation state of $Cu^{+3} = 3d^8$
Thus, Cu^{+3} (Oh) ,d^8
$KCuL_2$ oxidation state of $Cu = 1 + x - 4 = 0 \Rightarrow x = +3$
Cu^{+3} (d^8)



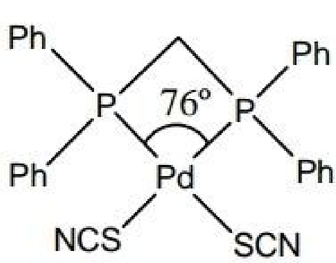
Hence, square planar low spin

121) **a**

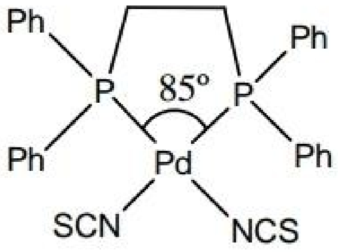
Mechanism of base hydrolysis can be given as
$[CoCl(NH_3)_5]^{+2} + OH^- \rightarrow [Co(NH_3)_4(NH_2)Cl]^{+1} + H_2O$

$[Co(NH_3)_4(NH_2)Cl]^{+1} \xrightarrow{\text{`ab}\quad\text{cde}} [Co(NH_3)_4(NH_2)]^{+2} + Cl^{-1}$

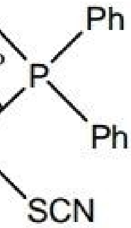
$[Co(NH_3)_4(NH_2)]^{+2} + OH^- \rightarrow [Co(NH_3)_5OH]^{+2}$



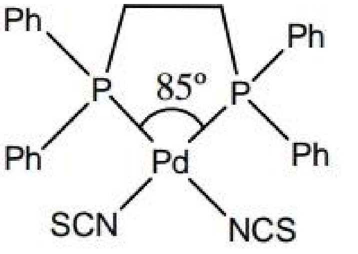
Small P–Pd–P angle, less
steric hindrance effective



Increase in P–Pd–P angle,increase in steric hindrance. No
effective π bonding from the P atom, the S atom of SCN⁻
l but due to steric hindrance SCN⁻

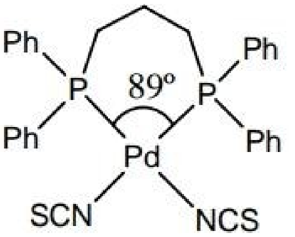


ngle, less
effective
ding



Increase in P–Pd–P angle,increase in steric hindrance. No
m of SCN⁻
ance SCN⁻

ance . No, effective π bonding from the P atom , the S
teric hindrance SCN^- binds through N atom.



P–Pd–P bond angle, further increase with increase in size of chelate ring and hence steric hindrance increases. No effective π bonding from P, the S atom of SCN⁻ can form the π bond but steric hindrance favours the Pd-N bonding

crease in size of chelate ring and hence steric hindrance increases .
om , the S atom of SCN^- ligand can form π bond but steric

For d^o (high spin) there is one spin allowed transition from $^5T_{2g} \rightarrow {}^5E_g$
In case of d^6 low spin commonly two spin allowed transitions are observed.
$^1A_{1g} \rightarrow {}^1T_{1g}$
$^1A_{1g} \rightarrow {}^1T_{2g}$
there are additional spin allowed transitions at higher energy but they are marked by allowed transitions. Hence, are not observed

124) b

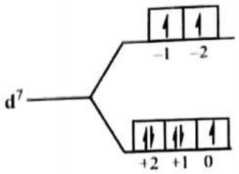
In I_3^- there is interaction between σ* a of I_2 and non-bonding electron of I^-. In case propanone and Br_2 there in interaction between σ* of Br_2 and non-bonding electron of propanone. Thus, both I_2 and Br_2 behave as acid.

125) c

Spin-orbit coupling is larger for the heavier atoms (Inner transition) and very small for lighter atoms.

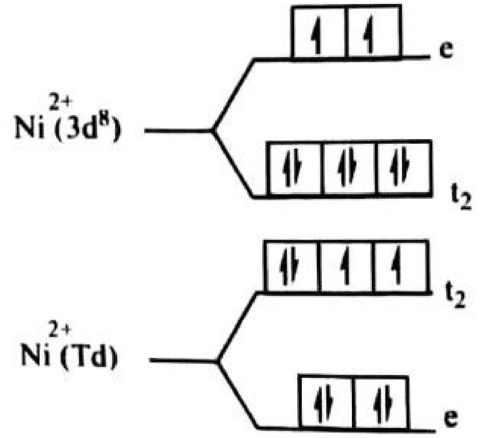
126) c

Co^{+3} (high spin) → $3d^7\ 4s^0$



S=1/2+1/2+1/2=3/2
L=4+2-0-1-2
L=3
Degeneracy for d-orbital = (2S+1)(2L+1)=(2x3/2+1)(2x3+1)=4×7=28

127) b



No. of unpaired electron = 2
μ_s = 2.9 B.M.
No orbital contribution

No. of unpaired electron = 2
μ_s = 4.1 B.M.

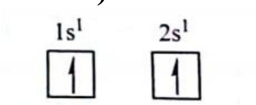
High value (4.1 B.M.) is due to μ_{spin}+ orbital contribution because t_2 is electronically degenerate

128) c

CrO_4^{-2}
$Cr^{+6} \rightarrow 3d^0\ 4s^0$
$O^{-2} \rightarrow 2s^2 2p^6$
MoO_4^{-2}
$Mo^{+6} \rightarrow 4d^0\ 5s^0$

In both Cr^{+6} and Mo^{+6} ions, there is no d-electrons, therefore, there is no d-d transition, since in both the ions. oxidation state is very high, there is LMCT in both cases. The energy gap between $2p^6$ (O^{-2}) and $3d^0$ (Cr^{+6}) is less than that between $2p^6$ (O^{-2}) and $4d^0$ (Mo^{+6}). Thus, LMCT energy
in CrO_4^{-2} is less (high λ_{max}) than that of MoO_4^{-2} (low λ_{max}).

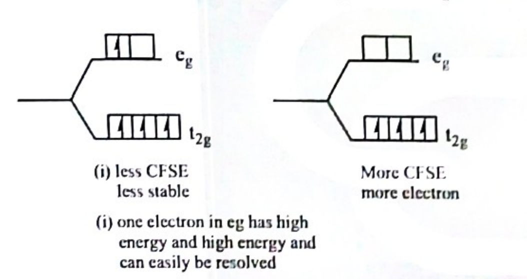
129) **c**



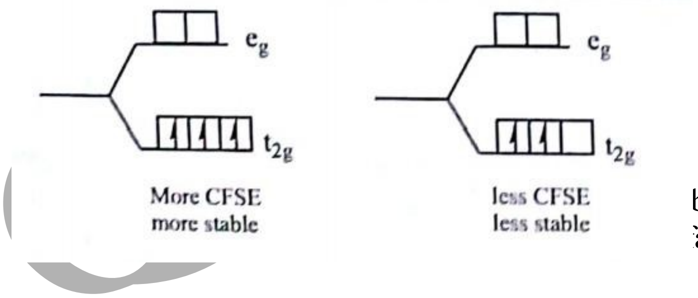
S=1/2+1/2=1
2S+1= 2x1+1=3
J=|l+s|...|l - s| = |1+0|...|1-0| =1
l=0 → S (term)
$^3S_1$

130) **c**

Electronic configuration of Cr =3d 4s
Electronic configuration of Cr^{+2} = $3d^4$
Electronic configuration of V^{+2} =$3d^3$
(A) Because of high nuclear charge of Cr is greater than that of V, Cr has higher. This ionization energy than V. Hence, Cr^{+2} is not easier to oxidized than V^{+2} in gas phase. Thus, option (a) is incorrect.
(B) Cr^{+2} (aq) →$[Cr(H_2O)_6]^{+2}$ →$[Cr(H_2O)_6]^{+3}$ +e^-



e^-
Thus, V (aq) does not easily oxidized
Thus, Cr^{+2} (aq) is more powerful reducing agent than V^{+2} (aq)



belongs to class1 metals and V^{+2} belongs to class 3
aster than V^{+2} (aq)

131) **d**

(I) $[Fe(CN)_6]^{-3} + [Co(CN)_5]^{-3} \rightarrow [(NC)_5Fe\text{-}CN\text{-}Co(CN)_5]^{-6}$
$$\xrightarrow{\text{electron transfer}} [Fe(CN)_6]^{-4} + [Co(CN)_5(OH_2)]^{-2}$$
(Inner sphere mechanism)

(II) $[Co(bipy)_3]^{+2} + [Co(bipy)_3]^{+3} \rightarrow [Co(bipy)_3]^{+3} + [Co(bipy)_3]^{+2}$
(outer sphere mechanism)

(III) $[Co(NH_3)F]^{+2} + [Cr(H_2O)_6]^{+2} \xrightarrow{H_2O} [(H_3N)_5Co^{III}\text{-}F\text{-}Cr^{II}(OH_2)_5]^{+4} \xrightarrow[+]{\text{electron transfer}}$
$[(H_3N)_5Co^{II}\text{-}F\text{-}Cr^{III}(OH_2)_5]^{+4} \xrightarrow{H_2O} [Co(NH_3)_5(OH)_2]^{+2} + [Cr(OH_2)_5F]^{+2}$
(Inner sphere mechanism)

Marcus equation is applicable only for cross-outer sphere reactions.
(B) is a self exchange reaction, its rate of electron transfer can be calculated experimentally.
No need to apply marcus equation.
(Reference basic inorganic chemistry by F.Albert Cotton, G Wilkinson and Paul L.Galls) third eddition.
In this question only (d) statement is correct.

132) **c**

For allowed transition : a)Spin multiplicity should be same or $\Delta S = 0$
b) $\Delta L = 0, \pm$,1for allowed transition
Therefore (4) is not allowed as $\Delta L \neq 0, \pm 1$
c) u → g **(**allowed**)**
g→ g **(** not allowed**)**
Therefore (1, 2) are not allowed
[+ → -] → forbidden so, therefore (1, 2) are not allowed
[+ → +] → allowed

133) **b**

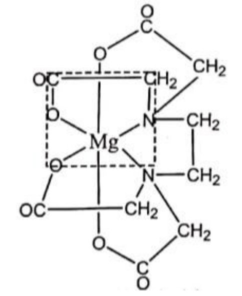
NO, I_2^-, Cu^{+2} and VO^{+2} is paramagnetic. Hence, EPR active where as I_2 is diamagnetic and EPR inactive.

134) **c**

$[Co(NCS)(NH_3)_5]^{+2} + [Fe(H_2O)_6]^{+2} \xrightarrow{H_2O} [(HN)_5Co\text{–}SCN\text{-}Fe(H_2O)_5]^{+4} \xrightarrow{\text{electron transfer}}$ -
$[(HN)_5Co\text{-}SCN\text{-}Fe(H_2O)_5]^{+4} \xrightarrow{H_2O} [Fe(SCN)(H_2O)_5]^{+2} + [Co(NH_3)_5(H_2O)]^{+2}$
Intermediate

$[Co(NH_3)_5(H_2O)]^{+2} \xrightarrow{+5H_3O^+} [Co(H_2O)_5]^{+2} + 5NH_4^+$
$[Fe(SCN)(H_2O)_5]^{+2} + H_2O \rightarrow [Fe(H_2O)_6]^{+3} + SCN^-$
Intermediate

135) **a**



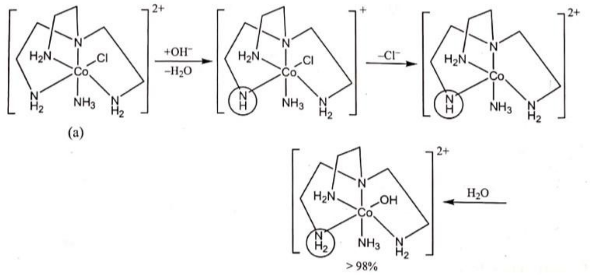
136) **a**

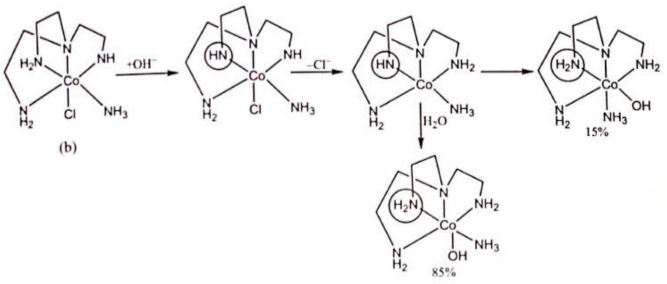
For strong Jahn-Teller distortion e_g orbital must be assymetrical filled.
$t^6_{2g}\ e^1_g$, $t^3_{2g}\ e^1_g$, $t^6_{2g}\ e^3_g$

137) a

The correct order of intensity of d-d transitions in the complexes follows order
cis-$[M(H_2O)_4Cl_2]$ > trans-$[M(H_2O)_4Cl_2]$ > $[M(H_2O)_6]^{+2}$

138) c





A react faster than B and B result in a mixture of product

139) b

As the oxidation state increases and size of central decreases ligand exchange rate decreases.

140) a

Electron transfer reactions by self-exchange electron transfer is fast when HOMO is π* and LUMO is also π* i.e. electron transfer is from a π*of reductant to the π* of oxidant.

(a) $[Ru(NH_3)_6]^{+2}$ + $[Ru(NH_3)_6]^{+3} \rightarrow [Ru(NH_3)_6]^{+3} + [Ru(NH_3)_6]^{+2}$ [Reaction is fast]
$(\pi^*)^6(\sigma^*)^0$ $(\pi^*)^5(\sigma^*)^0$
HOMO=$(\pi^*)^6$ LUMO=$(\pi^*)^5$
(b) $[Co(NH_3)_6]^{+2} + [Co(NH_3)_6]^{+3} \rightarrow [Co(NH_3)_6]^{+3} + [Co(NH_3)_6]^{+2}$ [Reaction is slow]
$(\pi^*)^5(\sigma^*)^2$ $(\pi^*)^6(\sigma^*)^0$
HOMO=$(\pi^*)^5$ LUMO=$(\sigma^*)^0$
(c) $[Cr(H_2O)_6]^{+2} + [Cr(H_2O)_6]^{+3} \rightarrow [Cr(H_2O)_6]^{+3} + [Cr(H_2O)_6]^{+2}$ [Reaction is slow]
$(\pi^*)^3(\sigma^*)^1$ $(\pi^*)^3(\sigma^*)^0$
HOMO=$(\sigma^*)^1$ LUMO=$(\sigma^*)^0$
(d) $[Fe(H_2O)_6]^{+2} + [Fe(H_2O)_6]^{+3} \rightarrow [Fe(H_2O)_6]^{+3} + [Fe(H_2O)_6]^{+2}$ [Reaction is fast]

$(\pi^*)^4(\sigma^*)^2$ $(\pi^*)^3(\sigma^*)^0$

HOMO=$(\pi^*)^4$ LUMO=$(\pi^*)^3$

Both reactions (a) and (d) are fast but reaction (a) is much faster than (d) because there is small change in M-L bond length in reaction (a) i.e. less activation energy is required

141) a

Hg^{+2} (aq) + X^-(aq) → $[HgX]^+$ (aq)

The stability constants for $[HgX]^+$ (aq) for X= F, Cl , Br follow the order: F < Cl < Br .Because Hg^{+2} is soft acid and Br^- is soft base.

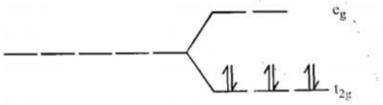
142) c

$[Mn(H_2O)_6]^{+2} \rightarrow t_{2g}^3\ e_g^2$: High spin complex

In this complex, there is neither orbital contribution nor temperature independent paramagnetism (No L-S coupling) and α =0. Thus, $\mu_{observed} = \mu_{spin}$

$[Co(H_2O)_6]^{+3}$ is a low spin complex.

$Co^{+3} \rightarrow d^6$ ie. $t_{2g}^6\ e_g^0$



No unpaired electron.

Therefore, it is diamagnetic in nature.

143) c

$Ti^{+3} \rightarrow d^1$ complex: $t_{2g}^1\ e_g^0$

Ti^{+3} complex exhibit one broad band due to

(i) Vibronic coupling

(ii) Jahn-Teller distortion

(iii) Spin-orbit coupling

$Co^{+2} \rightarrow d^7$ complex

Exhibit three broad bands due to following transitions:

$^4T_{1g} \rightarrow {}^4T_{2g}$; $^4T_{1g} \rightarrow {}^4A_{2g}$; $^4T_{1g} \rightarrow {}^4T_{1g}(P)$

•$Cr^{+3} \rightarrow d^3$ complex

Exhibit three broad bands due to following transitions:

$^4A_{2g} \rightarrow {}^4T_{2g}$; $^4A_{2g} \rightarrow {}^4T_{1g}(F)$; $^4A_{2g} \rightarrow {}^4T_{1g}(P)$

•Mn^{2+} complex→ d^5 complex exhibit a series of very weak (spin forbidden, Laporte forbidden and sharp bands).

•$Ni^{+2} \rightarrow d^8$ exhibit three broad bands due to following transitions:

$^3A_{2g} \rightarrow {}^3T_{2g}$; $^3A_{2g} \rightarrow {}^3T_{1g}(F)$; $^3A_{2g} \rightarrow {}^3T_{1g}(P)$

144) b

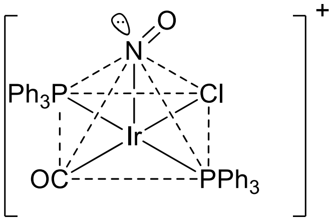
trans-$[CoLCl(en)_2]^+$ → A (on hydrolysis)

L= NO_2^-, NCS^-, OH^- ,Cl^-

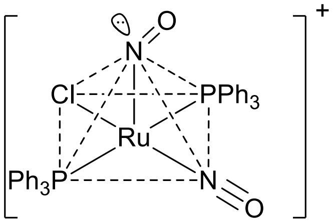
The tendency to form cis-isomer of the product (A) follows the order:

L= $NO_2^- < Cl^- < NCS^- < OH^-$

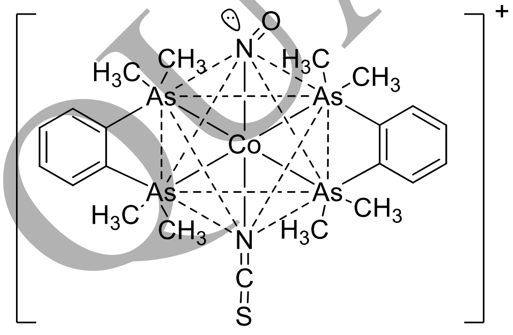
145) c



Ir = $9e^-$
PPh_3= $2e^-$ each
CO= $2e^-$
NO (bent) = $1e^-$ (lets consider)
$9e^- + 4e^- + 2e^- + 1e^- + 1e^- - 1e^- = 16e^-$
Considering NO in bent form gives TVE = 16, thus a square pyramidal structure of complex gains stability with 16 e^-, So we can say **NO present in bent mode**



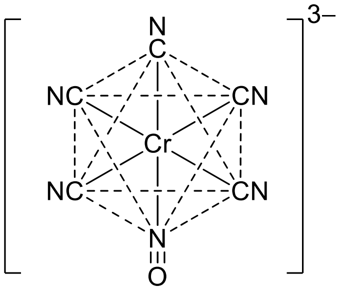
Ru= 8 e^-
PPh_3=2 e^- each
Cl= 1 e^-
NO(bent) = 1 e^-
NO(linear) = 3 e^-
$8e^- + 4e^- + 1e^- + 1e^- + 3e^- - 1e^- = 16e^-$
Considering one NO in bent form and another in linear gives TVE = 16, thus a square pyramidal structure of complex gains stability with 16 e^-, So we can say **One NO preset in bent mode and other in linear mode .**



Co = 9 e^-
AsR_3=2 e^- each
NCS=1 e^-
NO(bent)=1 e^-

$9e^- + 8e^- + 1e^- + 1e^- - 1e^- = 18e^-$

Considering NO in bent form gives TVE = 18, thus an octahedral structure of complex gains stability with $18e^-$, So we can say **NO present in bent mode**



Cr=6 e^-
CN= 1 e^- (each)
NO(linear) = 3 e^-

$6e^- + 5e^- + 3e^- + 3e^- = 17e^-$

Considering NO in linear form gives TVE = 17, thus an octahedral structure of complex gains stability with $18e^-$, So we can say **NO present in linear form** ($17e^-$ species is considered quite stable as on putting NO as bent, we were just getting $15e^-$, which would be too unstable)

146) b

An aqueous solution of Fe(III) ion (A) gives a blood-red colour on reaction with KSCN the blood red colour is due to formation of $\mathbf{[Fe(SCN)(H_2O)_5]^{+2}}$ (B). The colour may also used for the identification of Iron (III). This colour is destroyed by the addition of F^- ion due to the formation of $[FeF_6]^{-3}$ (C).

$[Fe(H_2O)_6]^{+3} + SCN^- \rightarrow [Fe(SCN)(H_2O)_5]^{+2} \xrightarrow{NaF} [FeF_6]^{-3}$
(A) (B) (C)
Blood red colour Due to LMCT
colourles , d-d transition ,laporte forbidden ,spin forbidden

147) b

In chlorophyll, visible absorption band arise from excitation of electron from the π-HOMO to π* LUMO, thus, has maximum value of molar extinction coefficient value.
$[NiCl_4]^{-2}$ is a tetrahedral comples, thus, p-d mixing will be there, hence, Laporte partially allowed and spin allowed transition.
In $[Cr(H_2O)_6]^{+2}$, d-d transition will be there. hence, Laporte forbidden and spin allowed transition.
In $[Mn(H_2O)_6]^{+2}$ transition is both Laporte and spin forbidden.
So, the order of molar extinction coefficient value is:
Chlorophyll > $[NiCl_4]^{-2} > [Cr(H_2O)_6]^{+2} > [Mn(H_2O)_6]^{+2}$

148) b

The base hydrolysis of $\mathbf{[Co(py)_4Cl_2]^+}$ is independent $\mathbf{OH^-}$ of concentration because there is no protonic hydrogen in the complex.

149) b

$FeCr_2O_4$ has normal spinel structure thus, Fe^{+2} occupy tetrahedral site. **$NiGa_2O_4$** has inverse spinel structure thus, Ni^{+2} occupy octahedral site.

150) c

cis-[Fe(phen)$_2$ (NCS-N)$_2$] (A) complex at high temperature (300K) exists as high spin with four unpaired electrons but when temperature is decreased, there is sharp decrease in magnetic moment at 174 K and complex becomes low spin. This indicates that at 174K, complex (A) exists as both high spin and low spin.

Thus, at 300K, complex A has four unpaired electrons.

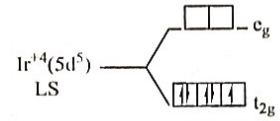
$\mu = \sqrt[u]{n(n+2)} = \sqrt[u]{4(6)} = \sqrt[u]{24} = 4.89$ BM

Complex [Fe(phen)$_3$]Cl$_2$ (B) at 300K is a low spin complex, thus have $t_{2g}^6\ e_g^0$ configuration ,hence no unpaired electron.

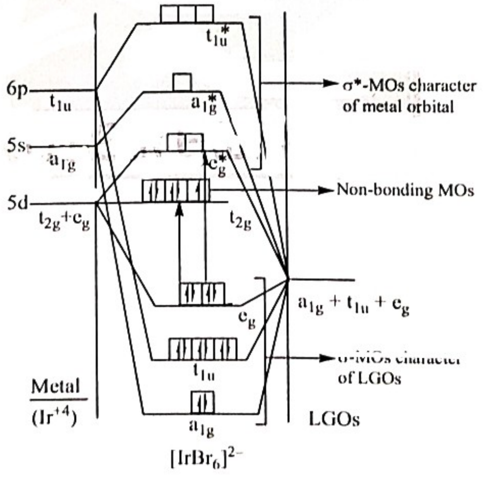
$\mu = \sqrt[u]{n(n+2)} = \sqrt[u]{0(0+2)} = 0$ BM

151) c

In $[IrBr_6]^{-2}$ oxidation state of Ir is +4 and Ir^{+4} is low spin. octahedral complex with the electronic configuration:



There are two charge transfer bands and their origin are ligand→ metal (σ →t_{2g} and σ →e_g)
as shown in the figure.



Other transitions are of high energy and do not observed.

152) c

$[*Co(NH_3)_6]^{+2}$ + $[Co(NH_3)_6]^{+3} \rightarrow [*Co(NH_3)_6]^{+3} + [Co(NH_3)_6]^{+2}$

High spin low spin

$t_{2g}^5\ e_g^2$ $t_{2g}^{\ 6}\ e_g^0$

Labile Inert

Co- NH_3 Co- NH_3 Bond length = 193.6pm

Bond length = 211.4pm

The rate of electron transfer for the reaction is very slow (second order rate constant $=10^{-6}$ L $mol^{-1}s^{-1}$) because of following reason :

• Low spin $[Co(NH_3)_6]^{+3}$ (configuration $t_{2g}{}^{6}\,e_g{}^{0}$) has all the metal -electrons pointing in between the ligands whereas, high spin $[{}^*Co(NH_3)_6]^{+2}$ (configuration $t_{2g}{}^{5}\,e_g{}^{2}$) has two e_g electrons pointing directly at the ligands. The electrons present in e_g orbitals cause more repulsion with ligands than that of t_{2g} electrons. Thus, M-L bond lengths in both complexes are different enough and more activation energy is needed to make them the same in transition state .

Also, no simple addition or removal of an electron can convert these configuration into one another. Thus, it is necessary to excite the oxidation states before the reaction can occur, as shown below:

$$^*Co^{+2}\,(t_{2g}{}^{5}\,e_g{}^{2}) \rightarrow (t_{2g}{}^{6}\,e_g{}^{1}) \xrightarrow{\text{‹q©to } t_{2g}} (t_{2g}{}^{5}\,e_g{}^{1}) \rightarrow (t_{2g}{}^{6}\,e_g{}^{0})\,{}^*Co^{+3}$$

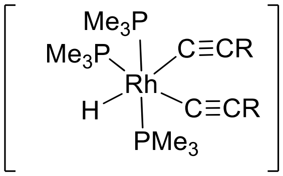
(electronic transition)

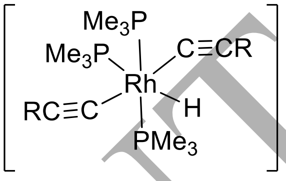
$$Co^{+3}\,(t_{2g}{}^{6}\,e_g{}^{0}) \rightarrow (t_{2g}{}^{5}\,e_g{}^{1}) \xrightarrow{\text{‹q©to } t_{2g}} (t_{2g}{}^{6}\,e_g{}^{1}) \rightarrow (t_{2g}{}^{5}\,e_g{}^{2})\,Co^{+2}$$

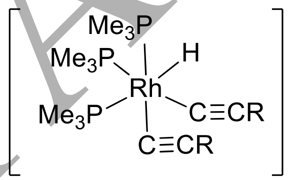
(electronic transition)

153) b

Geometrical isomers for complex **$[RhH(C{\equiv}CR)_2(PMe_3)_3]$** are







154) d

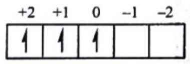
Solutions of **I_2**, in donor solvents such as pyridine, ethers, ketones, alcohol are brown or yellow due to formation of a charge transfer complex. Acetone or ethanol and similar compounds donate electron density through a σ lone pair to the σ* -orbital of iodine.

155) b

In the complexes, $[Fe(bpy)_3]^{+2}$, $[Ru(bpy)_3]^{+2}$ and $[Fe(phen)_3]^{+2}$, ligands bpy and phen have empty π* orbitals, thus, band in electronic spectra is due to metal to ligand charge transfer (MLCT). Whereas, the other complexes i.e. $[FeCl_4]^{2-}$ (220 nm), $[FeBr_4]^{2-}$ (244 nm), $[ReO_4]^{-}$ (227 nm) and $[TcO_4]^{-}$ (286 nm) show LMCT bands.

156) b

d^3-electronic configuration:



L=2+1+0 = 3 i.e. 'F'

S= 3 x 1/2 = 3/2

2S+1 = 2 x 3/2 + 1 = 4

J = less than half filled= L-S= 3-3/2 = 3/2
Thus, ground state term is = $^{2S+1}L_J = {}^4F_{3/2}$

157) **c**

$$[Co^{III}(NH_3)_5Cl]^{+2} + [Cr^{II}(OH_2)_6]^{+2} \xrightarrow{H_2O} \underset{\text{Inert}\qquad\qquad \text{Labile}}{[(NH_3)_5Co^{III}\text{–Cl–}Cr^{II}(H_2O)_5]^{+4}} \xrightarrow{\text{electron transfer-}}$$

$$\downarrow$$

$$\underset{\text{Labile}\qquad\qquad \text{Inert}}{[(NH_3)_5Co^{II}\text{–Cl–}Cr^{III}(H_2O)_5]^{+4}}$$

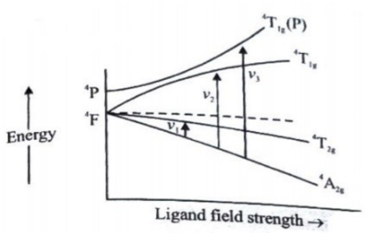
$$\downarrow$$

$$[Co(NH_3)_5]^{+2} + \underset{(B)}{[Co(H_2O)_5Cl]^{+2}}$$

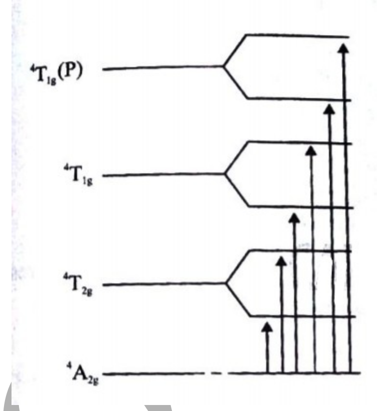
$$[Co(NH_3)_5]^{+2} + H_2O \rightarrow [Co(NH_3)_5(H_2O)]^{+2} \xrightarrow{+5H_3O^+} [Co(H_2O)_6]^{+2} + 5NH_4^+$$

158) **d**

In $[Cr(en)_3]^{+3}$, which is an octahedral complex, three spin allowed electronic transitions are observed.



Trans-$[Cr(en)_2F_2]^+$ is a tetragonal complex. Therefore, there is splitting of $^4T_{2g}$, $^4T_{1g}$, and $^4T_{1g}$ (P) states. $^4A_{2g}$ term does not split. Thus, 6 electronic transitions are observed.



159) **a**

The value of magnetic moment will be independent of temperature for $[Fe(acac)_3]$ because this complex is high spin with electronic configuration and the promotion of electron from t_{2g} to e_g or e_g to t_{2g} is spin forbidden with variation of temperature. Also, the high spin $[Fe(acac)_3]$ has ground state $^6A_{1g}$ and it has no excited states of the same spin multiplicity as that of the ground state.

160) **b**

$$\text{KNO}_2 \text{ in dil . AcOH} \xrightarrow{\text{Solid} \quad \text{Thiourea}} \text{N}_2 \text{ gas} \uparrow + \text{SCN}^- + \text{H}_2\text{O}$$

(P)

$$\downarrow \text{ dil FeCl}_3$$

$$[\text{Hg(SCN)}_4]^{2-} \xleftarrow[\text{solution}]{\text{°±\`{}²cdd} \quad \text{HgCl2}} [\text{Fe(H}_2\text{O)}_5\text{(SCN)}]^{2+}$$

Colourless (R) Blood red (Q)

161) **d**

$N_2^+ = \sigma^2_{1s}\ \sigma^2_{1s*}\ \sigma^2_{2s}\ \sigma^2_{2s}*\ \pi^2_{2px} = \pi^2_{2py}\ \sigma^1_{2pz}$

σ^1_{2pz} = gerade

$\Lambda = 0$ i.e. Σ

$S = ½$

$2S+1 = 2 \times 1/2 + 1 = 2$

As σ^1_{2pz} orbital is symmetric, (+) is used.

Thus, term symbol of N_2^+, is $\Lambda_{g/u} = {}^2\Sigma$

162) **c**

In the formation of $NaCl_2$ a very large second stage ionization energy is required as Na^+ already attain nearest noble gas configuration thus, the calculated heat of formation (ΔH_f) will be positive due to high value of I.E_2 of Na.

Ca shows +2 as stable oxidation state but it can release only a single electron easily (though it is less stable than Ca^{+2}). Thus, the calculated heat of formation (ΔH_f) will be negative for CaF.

163) Correct option (b)

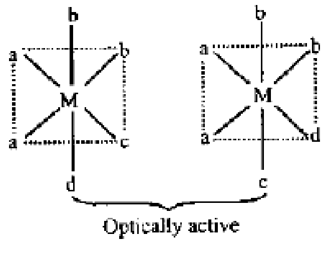
Steric hindrance favours dissociative substitution in octahedral complexes, hence statement (1) is correct

Higher charge on metal will not allow dissociation of existing ligand and will not favour acceptance of electron pair of entering ligands, hence statement (2) is incorrect

During dissociative substitution reaction a penta coordinated intermediate is observed, hence statement (3) is also correct.

Nature of entering ligand does not influence the reaction much, hence statement (4) is incorrect.

164.) Correct option (b)



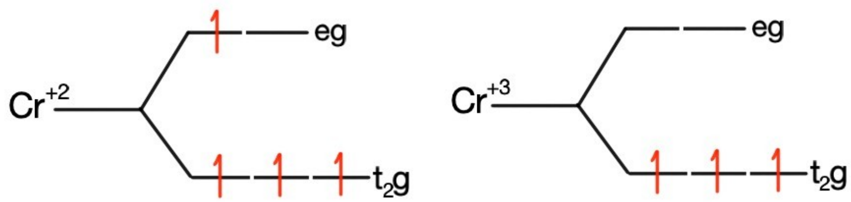
165.) Correct option (a)

Oxidation state of metals in $VO_{»}^{‘\$}$, $CrO_{»}^{q\$}$ and $MnO_{»}^{\$}$ are V(+5), Cr(+6) and Mn(+7) respectively,
Since, $\lambda_{ÀÁÂÃ} \propto Oxidation\ \ State\ \ of\ \ \ \ \ metal$
Thus preferred order will be, $VO_{»}^{‘\$} < CrO_{»}^{q\$} < MnO_{»}^{\$}$

As $\lambda_{ÀÁÂÃ}$ decreases on going down the group,
thus preferred order will be $WO_{»}^{q\$} < MoO_{»}^{q\$} < CrO_{»}^{q\$}$

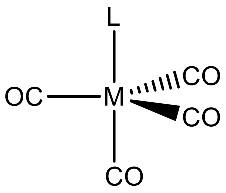
166.) Correct option (b)

Electron transfer between Cr^{+2}(d^4 system) and Cr^{+3}(d^3 system) takes place via Inner Sphere electron

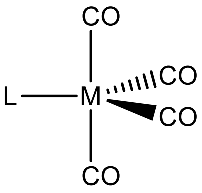


LUMO of Cr+3 (eg
is correct.
Statement B is correct as it involves large inner-sphere reorganization energy.
Statement C is incorrect as M–L bond lengths changes while inner-sphere electron transfer mechanism.
Rate of self-exchange electron transfer is always slow than cross-exchange electron transfer mechanism.

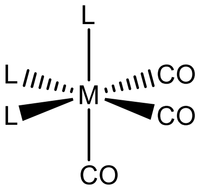
167.) Correct option (d)



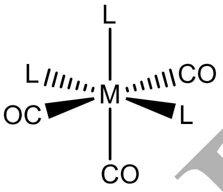
axial-M(CO)$_4$L
Point group C$_{3V}$
Number of IR Bands = 3



equitoial-M(CO)$_4$L
Point group C$_{2V}$
Number of IR Bands = 4



fac-ML$_3$(CO)$_3$
Point group C$_{3V}$
Number of IR Bands = 2

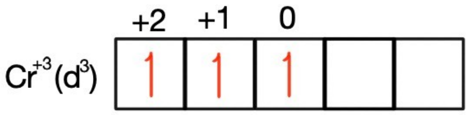


mer-ML$_3$(CO)$_3$
Point group C$_{2V}$
Number of IR Bands = 3

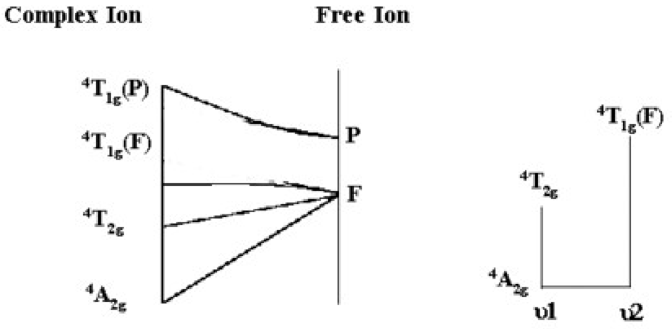
SHORT TRICK:

1. When point group is C$_{3V}$ then number of IR bands will be N-1, where N is number of CO ligands
2. When point group is C$_{2V}$ then number of IR bands will be N, where N is number of CO ligands

168.) Correct option (b)



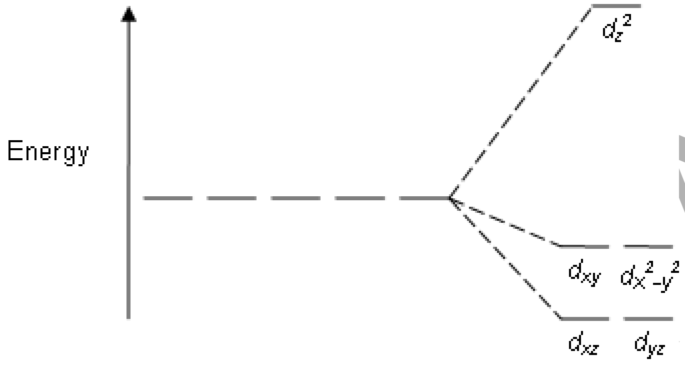
Ground State term symbol will be
$\sum m_\ell = +2+1+0=3$, thus term will be F
spin multiplicity = $2S+1 = 2\times\frac{‘}{q}+1 = 4$
Thus overall ground state term = ^{4}F
Now, according to Orgel diagram for d^3 system



169.) Correct option (d)

Point Group of Trigonal bipyramidal geometry is D_{3h}, as it has C_3 principle axis of rotation and $3C_2$ axes perpendicular to principle axis, also there is a horizontal plane.

The order of energies of d-orbitals for TBP geometry will be $d_{z2} > d_{x2-y2}, d_{xy} > d_{xz}, d_{yz}$



Trigonal bipyramidal

2

Organometallic Compounds

Hints & Solutions

1. Correct answer: (d)

Oxidation of metal is easier for electron rich systems, so electron rich metals undergo oxidative addition and as reduction is easier for electron-deficient metal, so it undergoes reductive elimination.

2. Correct answer (c)

This is correct stability order because $Ti(CH_2Ph)_4$ has no β-hydrogen .Hence no β -elimination and compound is stable whereas in $Ti(i\text{-}Pr)_4$ has max no of β -hydrogens followed by $TiEt_4$ and $TiMe_4$. So $Ti(i\text{-}Pr)_4$ undergoes fast β -elimination hence least stable.

$$Ti(i\text{-}Pr)_4 < TiEt_4 < TiMe_4 < Ti(CH_2Ph)_4$$

3. Correct answer: (b)

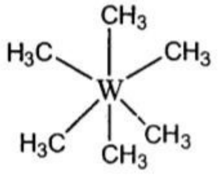
Compound	Number of electron in outer shell of central atom
$(\eta^5\text{-}C_5H_5)_2$ Fe	18
$(\eta^5\text{-}C_5H_5)_2$Co	19
$(\eta^5\text{-}C_5H_5)_2$Ru	18
$(\eta^5\text{-}C_5H_5)_2Co^+$	18

5 5 +

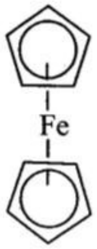
Oxidation (loss of electrons) of $(\eta^5\text{-}C_5H_5)_2$, Co to $(\eta^5\text{-}C_5H_5)_2$ Co^+ gives an 18 electron compound, (more stable) therefore easy to oxidise.

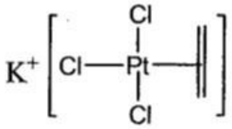
4. Correct answer: (a)

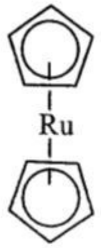
$W(CH_3)_6$ having 6 σ-bond with metal .



$W(CH_3)_6$







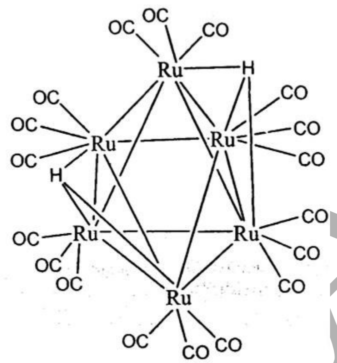
5. Correct answer: (c)

Ni+ 4CO →$Ni(CO)_4$

Fe+5CO→ $Fe(CO)_5$

Both Ni and Fe reacts directly with CO to give carbonyl compounds.

6. Correct answer: (d)



Electron cluster $H_2Ru_6(CO)_{18}$ displays a distorted octahedral metal geometry.

Here each hydride ligand is connected to 3-Ru atoms**.**

7. Correct answer: (a)

During hydroformylation the intermediate CH_3-CH_2-CH_2-$Co(CO)_4$ gets transformed to acyl intermediate $CH_3CH_2CH_2$ -$COCo(CO)_3$

8. Correct answer: (a)

Ziegler-Natta catalyst is **$TiCl_4$, $Al(C_2H_5)_3$**

9. Correct answer is (b).

M=V, x=6, z=1

i.e. $[V(CO)_6]^{-1}$ = 5+2x6+1=18

10. Correct answer is (d).

Because main group element follows octet rule.

$[Be(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)]$

2+5+1=8

11. Correct answer is (a)

12. Correct answer is (d).

$[CpFe(CO)(NO)]_2$

Step-1: Determine the total valence electron (TVE) = A

A=[5+8+2+3]x2=[18]x2=36

Step-2: B=(18n –A) where n number of metal.

B (2x18)-36 =36-36=0

No metal-metal bond found.

$[CpMo(CO)_3]_2$

Step-1: A [5+6+2x3] x2=[17]×2=34

Step-2: B= (18n-A)=2x18-34 = 36-34 = 2

Step-3: B/2 gives the total number of M-M bonds in the complex B =2/2=1

In this complex, the total number of M-M bonds is one

13. Correct answer is (a).

Order of donor ability **NMe_3** > **NH_3**> **pyridine**

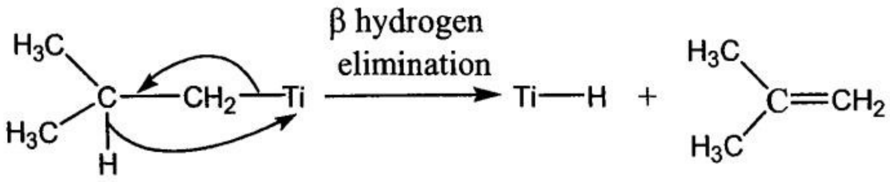
Order of CO stretching frequency **pyridine** > **NH_3** > **NMe_3**

14. Correct answer is (a).

Option A is Ruthenium(II) carbenoid complexes, also known as Grubb's Catalysts, they are widely used for olefin methathesis.

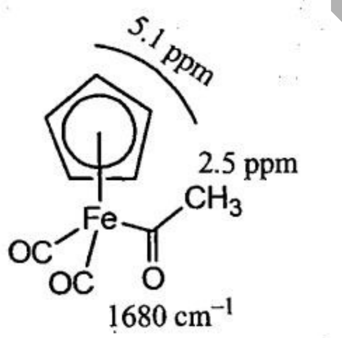
15. Correct answer is (b).

Compound A does not have any β hydrogen, hence β-hydride elimination is not possible in compound A, whereas compound B will undergo β-hydride elimination as follows



16. Correct answer is (a).

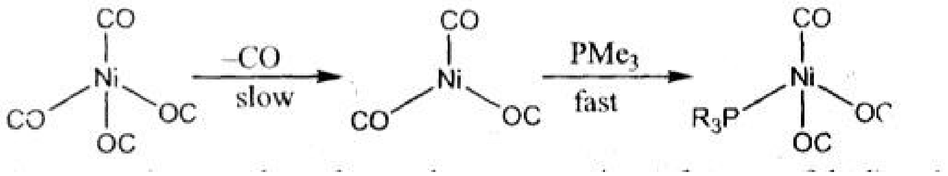
^{1}H-NMR giving one signal at 5.0ppm indicates presence of η^5-Cp ring, another one signal at 2.5ppm indicates presence of CH_3 group. IR band at 1680cm^{-1} indicates presence of ketone (C=O) group. Thus the appropriate structure of molecule.



17. Correct answer is (b).

$Ni(CO)_4$ Total valence electron around Ni 10+ 4x2=18 electron

Substitution reactions at coordinatively saturated tetrahedral complexes with a 18 electron count like **$Ni(CO)_4$**, or $Ni(CO)_2(PR_3)_2$ follows a simple first order kinetics.



Since rate does not depend upon the concentration and nature of the ligand suggesting a dissociative mechanism.

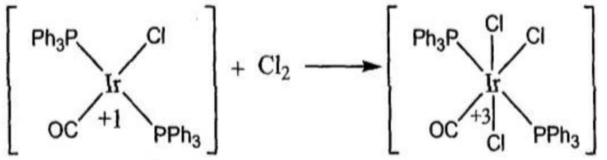
18. Correct answer is (b)

In **$[WO_4]^{-2}$, $[MoO_4]^{-2}$, $[ReO_4]^{-2}$ $[CrO_4]^{-2}$**all the metals have same oxidation state but Cr^{+6} is of smallest size. Therefore it has strongest tendency to attract electrons. Therefore strongest oxidizing agent.

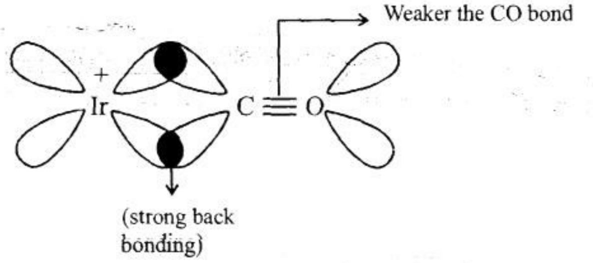
19. Correct answer is (a).

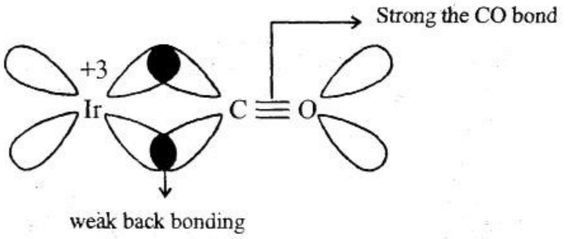
Since in product metal Ir is present in the higher oxidation state. So, there is less back bonding to orbital of CO.

34.



Since in product metal Ir is present in the higher oxidation state. So, there is less back bonding to

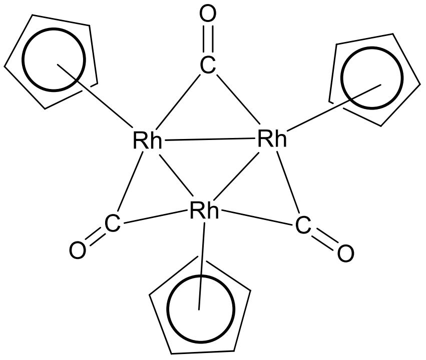




Hence, $\bar{\upsilon}$ (CO) product > $\bar{\upsilon}$ (CO) reactant

20. Correct option (b)

Triplet of carbonyl carbon indicates the each CO is attached with chemically equivalent two Rh atoms that means **μ_2**-CO complex. Actual structure is



21. Corret answer is (b)

[$Os_3(CO)_{12}$]

Step-1: Calculate T.V.E. (total valency electron)

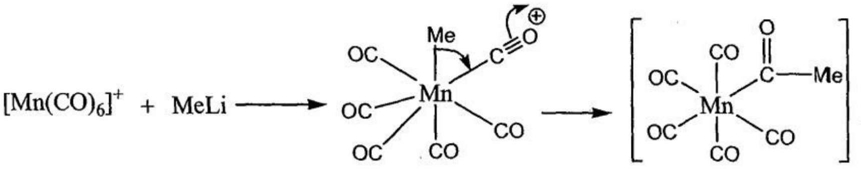
8x3 + 2×12 = 48

Step-II: Polyhedral electron count

T.V.E - (nx12) = 48-36=12 n=number of the metal atom

Step-III: =P.E.C./2=12/2 =6 = (n+3) =Archano.

22. Correct answer is (d).



23. Correct answer is (b).

Because metal carbonyls are stronger bond , to break this bond huge amount of energy are required. But metal-metal bonds are weaker bond. So, reaction is endothermic and enthalpy predominant and entropy unfavourable.

24. Correct answer is (d).

[(η^5 –C_5H_5)RuCl(CO)(PPh_3)]

T.V.E = 5+8+1+2+2=18e^-

[$W(CO)_3(SiMe_3)(Cl)(NCMe)_2$]

T.V.E= 6+ 6+1+1+ 2x2 =18e$^-$

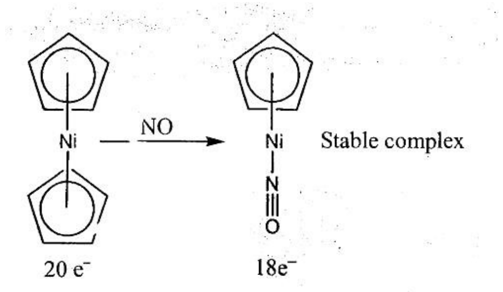
[IrCl$_3$(PPh$_3$)$_2$(AsPh$_2$)]$^-$

T.V.E= 9+ 3 +4+1+ 1 =18e$^-$

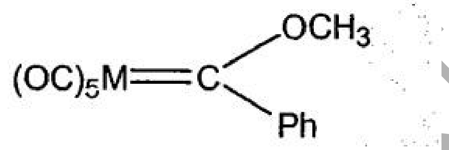
[Os(N)Br$_2$(PMe$_3$)(NMe$_2$)]$^-$

T.V.E= 8+ 5 +2+1+ 1 =17e

25. Correct answer is (c)



26. Correct option (a)



ELECTRON COUNT = 2x5 +M+2 =18

M = 18-12 =6

So, M = Cr, Re$^+$

27. Correct answer is (a).

As the π-accepting abilities of phosphine increases ν_{C-O} stretching frequency of the complex increases. So, the order of n-accepting abilities among the given phosphine is:

PF$_3$ > PCl$_3$ > PClPh$_2$ > PMe$_3$

i.e. A>B>C>D.

So, the correct combination for ν_{C-O} stretching is:

A→2090

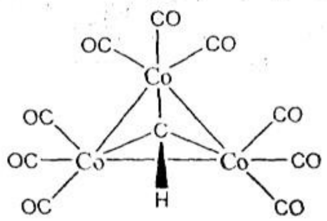
B→ 2040

C→ 1977

D→ 1945

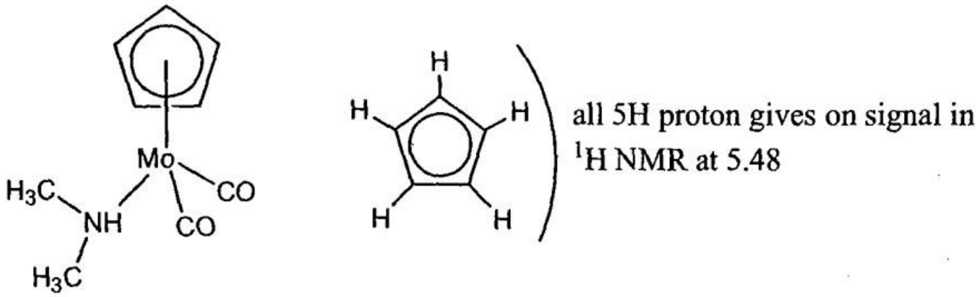
28. Correct answer is (a)

The structure of cluster $[Co_3(CH)(CO)_9]$



So, the number of M-M bond = 3 and bridging ligand=1 CH

29. Correct answer is (a)



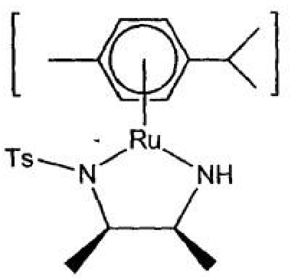
all 5H proton gives on signal in ^{1}H NMR at 5.48

Since, the molecule is C_2 -symmetric. So, two CO's will give two absorption band in IR spectrum.

30. Correct answer is (b)

$[Rh(CO)_2I_2]^{-1}$ → Hydroformylation.

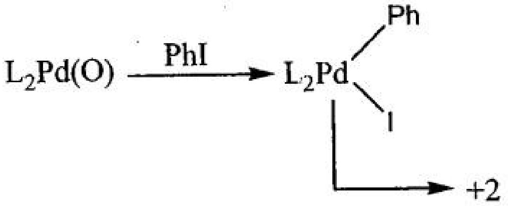
$[Pd(PPh_3)_4]$ →Heck coupling (It is a catalyst for Heck coupling)



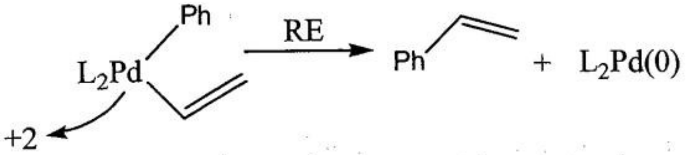
→ Asymmetry hydrogen transfer.

31. Correct answer is (a).

Step (A) is O.A. because the oxidation state of the metal is increased by two units.



Step(B) is transmetallation because the ligand is transferring from one metal to another metal. Step(C) is reductive elimination because the oxidation state of the metal is increased by two units



32. Correct answer is (d)

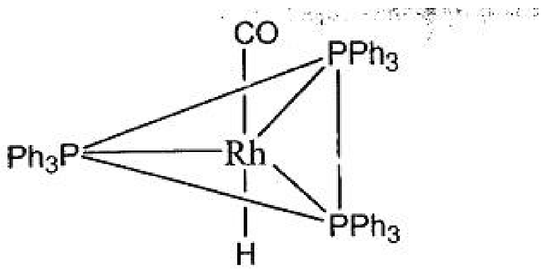
(a)[Rh(CO)$_2$I$_2$]$^-$ →16e$^-$ and a better coordinate for O.A.

(b) [Ir(PPh$_3$)$_2$(CO)Cl] →16e$^-$ species (Vaska's complex) O.A. is possible.

(c) [(η2-CpRu(CO)$_2$] →16e$^-$ system O.A. is not possible because metal in high oxidation state.

(d) [(η5 -Cp$_2$Ti(Me)Cl] →18e$^-$ species as such O.A. is not possible but after the dissociation of ligand 'CO', O.A. is possible.

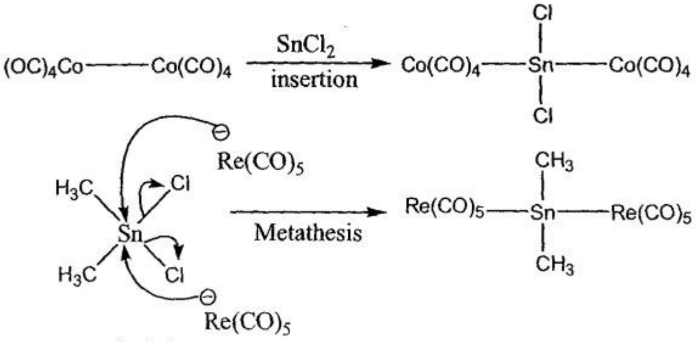
33. Correct answer is (b).



18 electron species in excess PPh_3 it becomes 20 electron species but the active catalyst is 16 electron species. So, in presence of excess PPh_3 the rate of hydroformylation will be decreases.

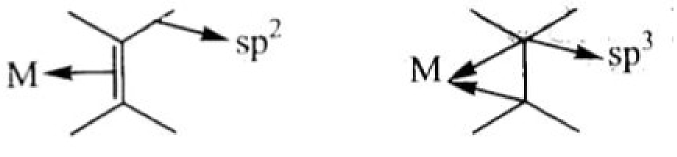
34. Correct answer is (a).

Since $SnCl_2$ will behaves as a carbene and it insert into the M-M bond. So, it is a kind of insertion reaction.



35. Correct answer is (c).

In Metal-Olefin interaction, the extent of increase in metal → Olefin л-back donation would strengthen the Metal-Olefin bond which produces a increase in C = C bond length and somewhat single bond character which results a change in hybridisation from sp² to sp³.



36. Correct answer is (c).

[(η7- tropylium)Mo(CO) $_3$]

In zero oxidation state of Mo, complex have 18 e^{-1} (stable)

7 +6+6 -1 = 18

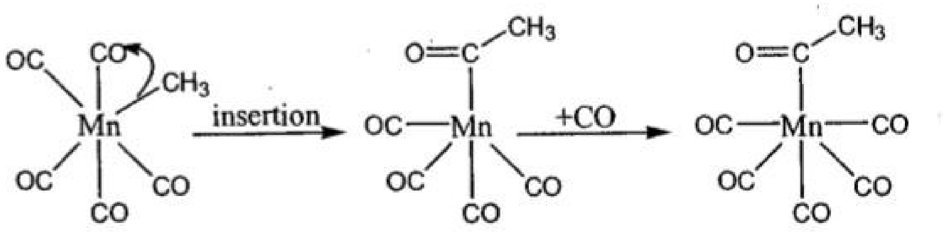
tropylium is a 7e- donor ligand in neutral method and +1 oxidation state

oxidation state of Mo = +1+x +0 = +1

x= 0

37. Correct answer is (d)

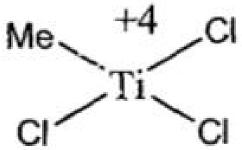
The above reaction is an example of 1,1-migratory insertion



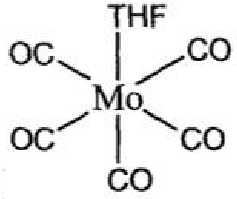
Insertion reaction

38. Correct Answer (C)

Since $MeTiCl_3$ have no electrons for back donation with л-accepting ligands like PMe_3 and CO, therefore, It reacts in order $NMe_3 > PMe_3 > CO$



Now, in (CO), Mo(thf), Mo have sufficient e-s and vacant site to react with л-acceptor ligand. Thus, the order is $CO > PMe_3 > NMe_3$



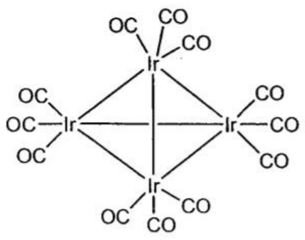
39. Correct answer is (c)

Total valency electron 12+18=30 (A) [(OPh) in bridging donate 3 electron]

B = (n×18 - A) = 36-30=6

Metal-metal bond = B/2 = 6/2=3 Correct answer is (c)

40. Correct answer is (b)

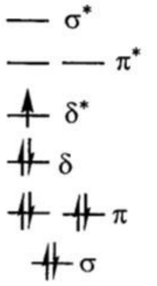


A= TVE =60

B (n×18) – TVE= 72 – 60= 12

metal-metal bond= B/2 =12/2= 6

41. Correct answer is (b)



$\left[Re_2Cl_4(PMe_2Ph)_4\right]^+$

$C = M + L$

$+1 = 2M - 4$

$\therefore \quad 2M = 5$

Total valence electron $= 14 - 5 = 9 \quad (\because 2M = 2 \times 7 = 14)$

M = Number of valence electron present in the metal

Bond order = $\frac{RSFRT}{U} = \frac{VFW}{U} = 3.5$

42. Correct answer is (d)

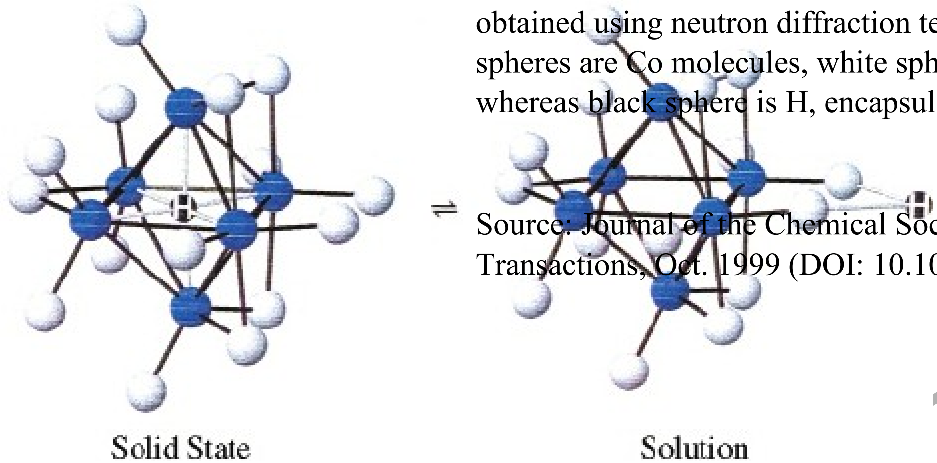
$HCo(CO)_4$, $HCo(CO)_3PBu_3$, $HRh(CO)(PPh_3)_3$. These all are the catalyst for hydroformylation process.

43. Correct answer is (b)

$H_3CoRu_3(CO)_{12}$ = 3+9+8×3+12×2 = 60 electron

44. Correct answer is (a)

[(H)Co_6 (CO) $_{15}$] has H encapsulated.

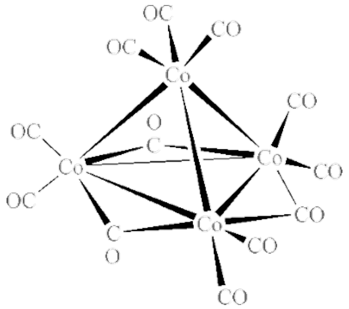


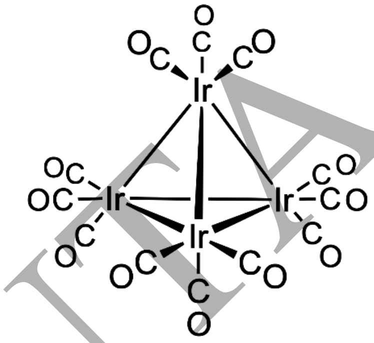
The image shows solid state structure of $HCo_6(CO)_{15}$, obtained using neutron diffraction technique. The blue spheres are Co molecules, white spheres are CO ligands whereas black sphere is H, encapsulated in the crystal.

Source: Journal of the Chemical Society Dalton Transactions, Oct. 1999 (DOI: 10.1039/a810025j)

45. Correct answer is (d)

Due to increase in size of Ir, compared to Co, the Metal-Metal bond length also increases, thus the ability to form bridge carbonyl decreases with increase in M-M bond



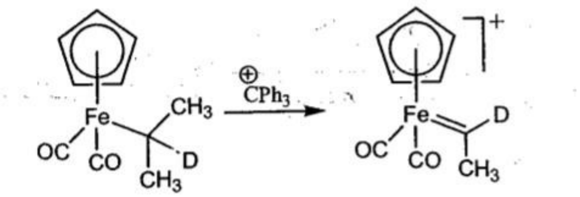


No of bridging CO= 3	No of bridging CO = 0
No of Terminal CO= 9	No of terminal CO =12

46. Correct answer is (d)

Explanation:

The electrophilic attack of Ph_3C on the given compound, results in removal of one Methyl group from $CDMe_2$ ligand, thus forming an alkene. Since the reacting species is 18 electron compound, after reaction, the final product A is also an 18e species.



$5+8+4+1 = 18$

47. Correct answer is (a)

$CH \rightarrow 4+1=5e$

$Co(CO)_3 \rightarrow 9+6=15e$ $CH \longleftarrow\!\!\!-\!-\!-\!-\!-\!\!\!\longrightarrow Co(CO)_3$

X

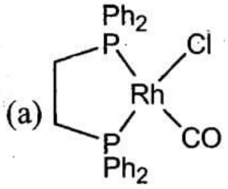
But, $CH_2 \rightarrow 4+2=6e$

$Ni(CO)_2 \rightarrow 10+4=14e$ not isolobal

48. Correct answer is (c)

In case of (c) the chances of conversion of heptacity from $\eta^5 \rightarrow \eta^3$ is more due to partial bond fixation. Others will not undergo change in heptacity, to retain their aromatic properties.

49. Correct answer is (a)



IR band at 1985 cm^{-1} indicates terminal CO. Both P atoms are non-equivalent. Each P atom will show doublet of doublet with ($^1J_{PRh}$ and $^2J_{pp}$).

50. Correct answer is (b)

106. $Fe_3(CO)_{12} \xrightarrow{RT} [Fe(CO)_4]^{-2}$

$8+8+2=18$ electron

$[Fe(CO)_4]^{-2}$ is isoelectronic with $Ni(CO)_4$

51. Correct answer (b)

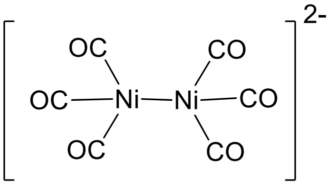
$[(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)Fe(CO)_2] \rightarrow [(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)Fe]$ (at temp range = 221-298K)

52. Correct answer is (c)

Most commonly the metal in the complexes in their low oxidation state with d^8 or d^{10} configuration undergo oxidative addition.

53. Correct answer is (c)

Oxidation state of Ni in complex $[Ni_2(CO)_6]^{2-}$

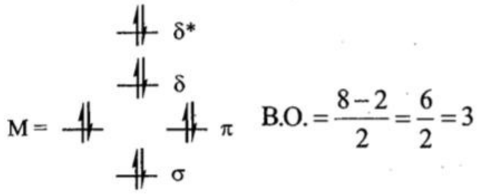


2x+0 = -2

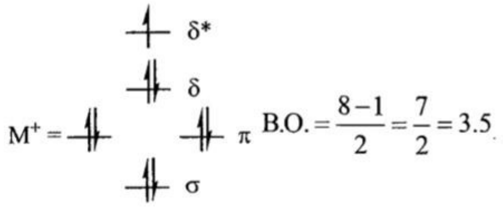
x=-2/2 , x = -1

M-M bond =1

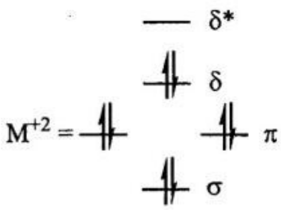
54. Correct answer is (a)



$$B.O. = \frac{8-2}{2} = \frac{6}{2} = 3$$



$$B.O. = \frac{8-1}{2} = \frac{7}{2} = 3.5$$



$$B.O. = \frac{8}{2} = 4$$

55. Correct option (a)

$[Fe_3(CO)_{15}C)]$

Total valency electron= 8x5+ 15x2+4=74

PEC=TEC- n×12

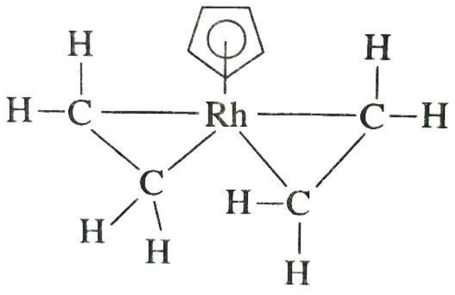
PEC =74-5×12= 74-60=14

PEC/2 =14/2 = 7

7=n+2

=5+2=(n+2) Nido where n=no. of metal in electron

56. Correct answer is (a)



$[\eta^5\text{-}C_5H_5Rh)(C_2H_4)_2]$ at -20°C shows a typical AA' XX' pattern in the olefinic region due to free rotation of the ethylene ligand about the metal-olefin bond

57. Correct answer is (c)

$Co(CO)_3$ 15 electron

R_2Si 6 electron (not isolobal)

$Mn(CO)_5$ 17 electron

CH_3 7 electron (not isolobal)

$Fe(CO)_4$ 16 electron

O 6 electron (isolobal)

$Mn(CO)_5$ 17 electron

RS 7 electron (isolobal)

58. Correct answer is (c)

$[(\eta^x\text{-}C_6H_6)Ru(\eta^y\text{-}C_6H_6)]$

x = 4, y = 6

$[(\eta^4\text{-}C_6H_6)Ru(\eta^6\text{-}C_6H_6)]$

Total electron 4+8+6 =18 electron. (Diamagnetic complex)

59. Correct answer is (b)

$Ni(CO)_4 + PPh_3 \xrightarrow{\Delta} [Ni(CO)_3(PPh_3)] + CO$

($18\ e^-$)

Since $Ni(CO)_4$ follows 18 electron rule. So, it follow substitution via dissociation mechanism i.e.

Step-1: $Ni(CO)_4 \rightarrow Ni(CO)_3 + CO$ (slow)

($18\ e^-$)

Step-2: $Ni(CO)_3 + PPh_3 \rightarrow Ni(CO)_3(PPh_3)$

($16\ e^-$)

So, the rate of reaction depends upon the concentration of $Ni(CO)_4$ only because this step is slowest step.

60. Correct answer is (b)

$H_3C\text{-}CH{=}CH_2 + CO + H_2 \rightarrow +H_3C\text{-}CH_2\text{-}CH_2\text{-}CHO$ (butanal)

in presence of $Co_2(CO)_8$ as a catalyst

[Hydroformylation.]

61. Correct answer is (*), none of the given option is correct .

62. Correct answer is (b)

$Co_4(CO)_{12}$

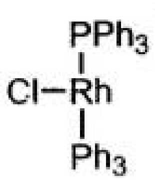
TVE =36+ 24 = 60

PEC=TVE-(nx12)=60-48=12

PEC/2=12/2 = 6 = 4+2 (n+2=Nido)

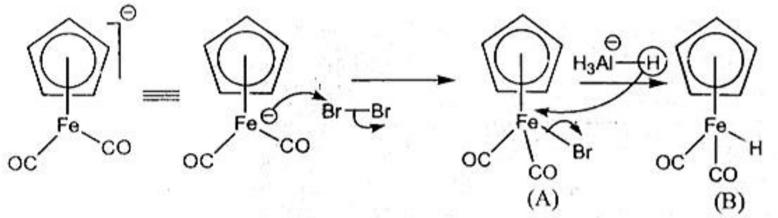
63. Correct answer is (a)

$Rh(PPh_3)_3Cl$ is a Wilkinson catalyst in hydrogenation step one PPh_3 loss due to steric factor and form $Rh(PPh_3)_2Cl$



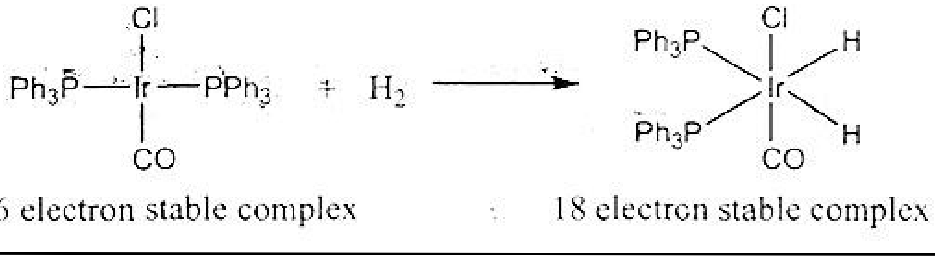
Shape = T-shaped

64. Correct answer is (a)



So, in the product (B) it shows two signals in ^1H NMR one for 5H of Cp ring and one for Fe-H proton with intensity ratio 5: 1.

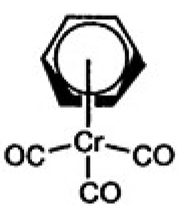
65. Correct answer is (c)



16 electron stable complex 18 electron stable complex

$[IrCl(CO)(PPh_3)_2]$ is a 16 electron complex called as Vaska complex. Only show oxidative addition in the presence of $\mathbf{H_2}$

66. Correct answer is (a)



All given options are incorrect except (a) as there is **ring current disruption** after formation of complex in $\mathbf{[(\eta^6\text{-}C_6H_6)Cr(CO)_3]}$ .The shift in δ is attributed to this reason from **7.2 ppm to 4.5 almost .**

67. Correct answer is (b)

The $\mathbf{C_2B_9H_{12}}$ is carborane anion.

$\mathbf{C_2B_9H_{12}^{-1}}$ follow wade rule as

$C \equiv BH$

$\downarrow \quad \downarrow$

$(4e^-)$ $(4e^-)$

$\mathbf{C_2B_9H_{12}^{-1}} \equiv (BH)_2B_9H_{12}^{-1} \equiv B_2H_2B_9H_{12}^{-1} \equiv B_{11}H_{14}^{-1}$

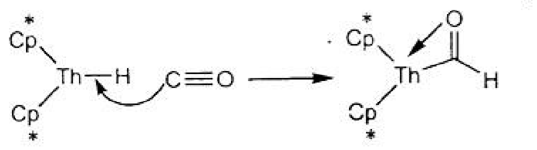
Now, $B_{11}H_{14}^{-1}$ is equivalent to $B_{11}H_{15}$ neutral borane which follows the formula $B_nH_n^{-4}$

which is the general formula of nidoborane.

$B_{11}H_{14}^{-1} \equiv B_{11}H_{15} \equiv B_nH_n^{-4} \equiv$ Nido.

68. Correct answer is (d)

It is a kind of insertion reaction of M-H (metalhydride bond between CO)



69. Correct answer is (a)

Complex (A) **$HM(CO)_5$ =1 + 7+ 10 =18 electron**

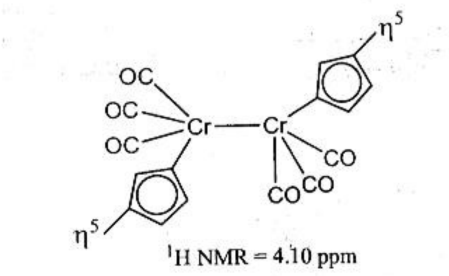
M=Mn [7 electron]

1 + 7+ 10 =18 electron

Complex (B) **$[(\eta^5\text{-}C_5H_5)M'(CO)_3]_2$**

$[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ **M'**=Cr=6 electron

10+12+12+2 (M-M) bond = 36 electron.



^{1}H NMR = 4.10 ppm

70. Correct option is (c)

$[Co(CO)_3(NO)]$ NO in linear form donate (3 electron.)

↓ ↓ ↓

9 + (2x3) +3= 18 electron

$[Ni(\eta^5\text{-}Cp)(NO)]$

↓ ↓ ↓

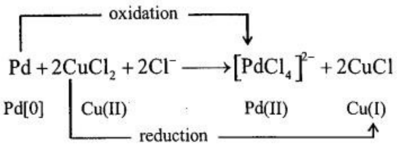
10 + 5 + 3 = 18 electron

In both complexes NO donating three electron. So, NO is in linear form.

71. Correct option is (a)

$[PdCl_4]^{-2}+C_2H_4+H_2O$ $CH_3CHO+Pd+2HC1+2Cl^-$

Pd(II) Pd(0)

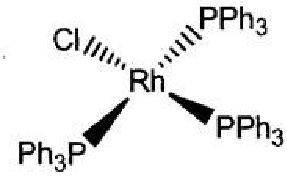


$2CuCl_2 + 1/2\ O_2 + 2HCI \rightarrow 2CuCl_2 + H_2O$

72. Correct option is (b)

73. Correct option is (a)

The refluxing of $RhCl_3$.3H,O with an excess of PPh_3, in ethanol gives a complex **$RhCl(PPh_3)_3$** is Wilkinson catalyst and common method for preparation of **$RhCl(PPh_3)_3$** is refluxing of **$RhCl_3.3H_2O$** with PPh_3.Moreover, on counting the total valence electrons, **$RhCl(PPh_3)_3$** = [9+3x2+1] = 16e.{Cl atom cannot be bridging, its contribution is 1}. Wilkinson catalyst is 16e$^-$ species.



It is a square planer 16-electron complex. Valence electron counting on rhodium metal centre.

(i) there is no overall charge on complex
(ii) there is one anionic ligand (Cl^-)
(iii) Rh metal atom must have +1 charge to compensate for the one negatively charged ligand. So, the oxidation state of Rh is +1.

74. Correct option is (a)

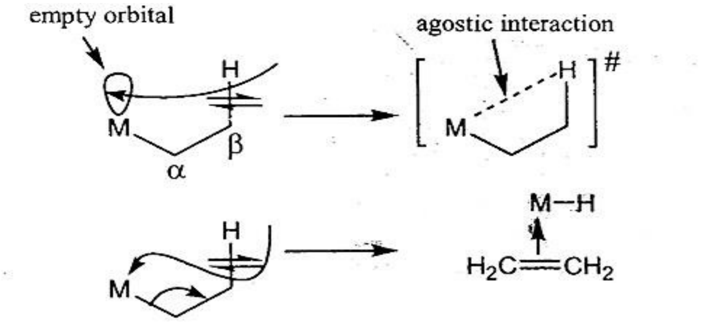
β-hydrogen elimination mechanism.

Since C-H, σ bond pair electron donate to the metal for this elimination. Therefore, as the donor ability of the σ electron pair increases rate of β-elimination increases.

In option D, the unit is anti-periplanar and thus β-H elimination not possible.

For β hydride elimination reaction β hydrogen should be closer to metal in option B,C all hydrogen atoms are far so elimination not possible (sp^2 carbon)

So, more facile β-elimination occur in option (a)



Electron donor ability at a bond is C-H (sp^3) > C-H (sp^2) >C-H (sp)

So, more facile β-elimination occur in option (a)

75. Correct option is (a)

The reaction follows SN, CB mechanism in which M-Y bond is fully broken before M-X bond begins to form.

Thus, Id mechanism is the most evidential mechanism.

76. Correct option is (a)

$[B_{12}H_{12}]^{2-} \equiv [B_nH_n]^{2-}$

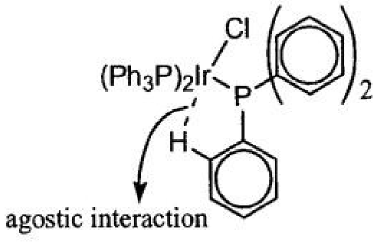
Therefore, it is closo structure

77. Correct option is (a)

$SbCl_3 + 3EtMgBr \rightarrow SbEt_3 + 3MgBrCl$

$2SbEt_3 + SbI_3 \rightarrow [Sb(Et)I_2]_n + SbEt_2I$

78. Correct option is (c)



Due to this agostic interaction C-H bond becomes weak and hydrogen flanked in between M and C.As proton come in contact with metal becomes shielded and upfield shift in ^{1}H NMR.

Since v $\propto \sqrt{K}$,bond strength of C-H bond decreases, in IR spectrum shift to lower wave number.

79. Correct option is (a)

Suzuki coupling-Palladium catalyzed cross coupling between organoboranic acid and halides.

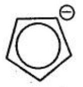
Heck coupling-Palladium catalyzed C-C coupling between aryl halides or vinyl halides and activated alkenes in the presence of a base.

Sonogashira coupling-This coupling terminal alkynes with aryl or vinyl halides is performed with a palladium catalyst, Cu(I) cocatalyst and amine base.

Negeshi coupling-This reaction is the organic reaction of an organohalide with an organic-zinc compound Pd and Ni catalyst.

80. Correct option is (a)

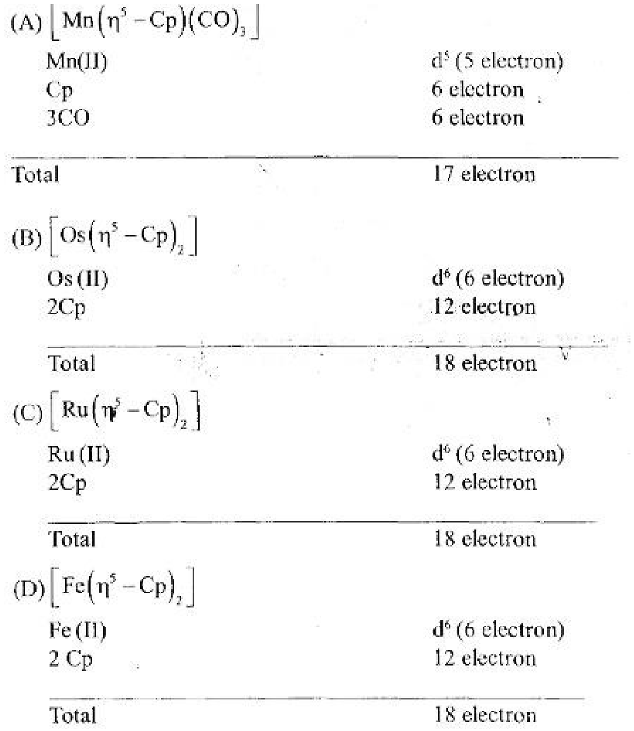
Here, Cp is cyclopentadienyl ligand is one of the most common and popular ligands in organometallic chemistry.



6 electron donor

It is an anionic ligand that normally coordinates in an **η^5** mode as a 6 electron donor.

Now, 18-electron rule apply on the complexes



(A) $\left[Mn(\eta^5-Cp)(CO)_3\right]$

Mn(II)	d^5 (5 electron)
Cp	6 electron
3CO	6 electron
Total	17 electron

(B) $\left[Os(\eta^5-Cp)_2\right]$

Os (II)	d^6 (6 electron)
2Cp	12 electron
Total	18 electron

(C) $\left[Ru(\eta^5-Cp)_2\right]$

Ru (II)	d^6 (6 electron)
2Cp	12 electron
Total	18 electron

(D) $\left[Fe(\eta^5-Cp)_2\right]$

Fe (II)	d^6 (6 electron)
2 Cp	12 electron
Total	18 electron

[Mn(η^5-Cp)(CO)$_3$] does not follow 18-electron rule. So, this complex is most deshielded compound when we are going 3d to 4d and 4d to 5d series in the transition element the shielding effect decrease because of the electron density or the distance between metal to ligand, increases. So, [Fe(η^5-Cp)$_2$] is more shielded than other.

Thus, the compound D is most shielded and compound A is most deshielded.

81. Correct option is (b)

[$Ru_6(C)(CO)_{17}$]

TEC =8x6+4+17x2 = 86

PEC= 86 - 6x12 = 14

PEC/2= 14/2 = 7

Therefore, 7=6+1=(n+1) closo

[$Os_5(C)(CO)_{15}$]

TEC= 8x5+4 +15x2 = 74

PEC =74-12x5

PEC = 74-60= 14/2 =7= (5+2)=(n+2) .Therefore, nido

[$Ru_5(C)(CO)_{16}$]

TEC= 8x5+4+16×2

TEC=76

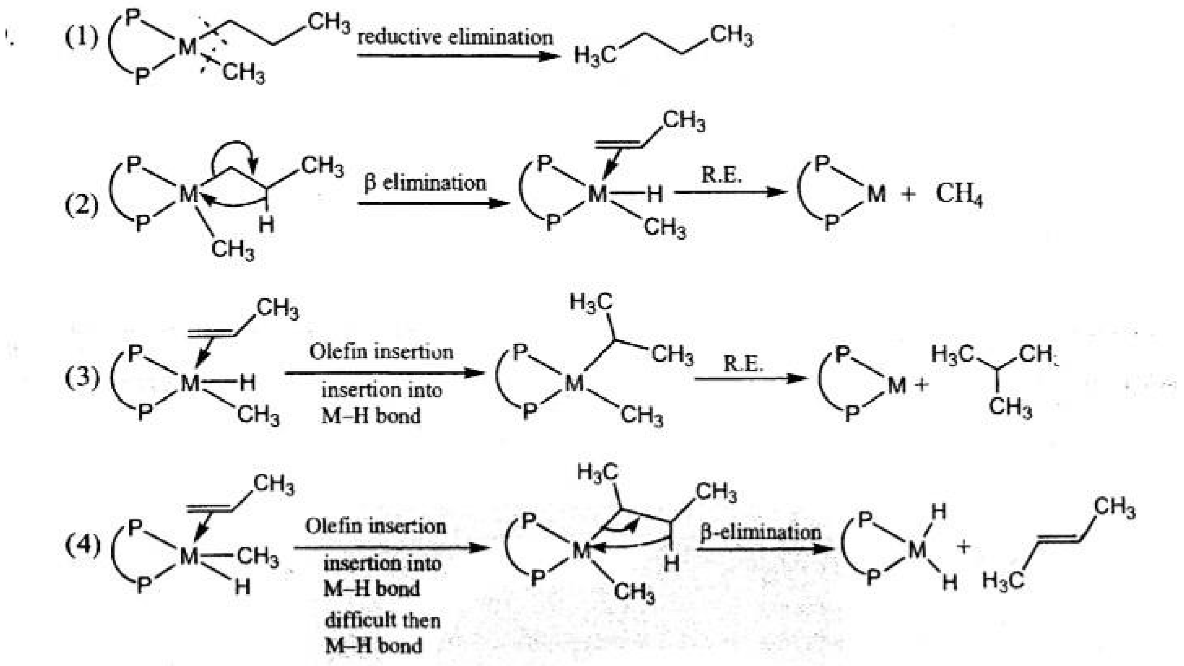
PEC =76-60=16

PEC/2=16/2 =8= (5+3)=(n+3) Arachno

82. Correct option is (a)

For reductive elimination, the eliminating group should be electron releasing group and also the eliminating product should be neutral.So, only Me group is electron releasing group among all the given option.

83. Correct option is (C)



All the products are possible but possibility of (4) is least as alkene doesnot undergo reductive elimination reaction easily as compare to alkane.

84. Correct option is (d)

alkyne can act as a 2 or 4electron donor .

Step-1 (**ϭ** -bond formed)

L(π)→ M(ϭ)

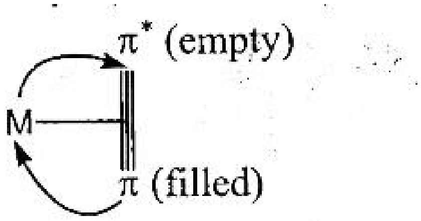
From filled acetylene **π** orbitals to empty metal d orbital

Step-2 (**π** -bond formed)

M(π)→ L(π*)

From filled metal d orbital to empty acetylene **π*** orbitals

Correct option is (d)



85. Correct option is (d)

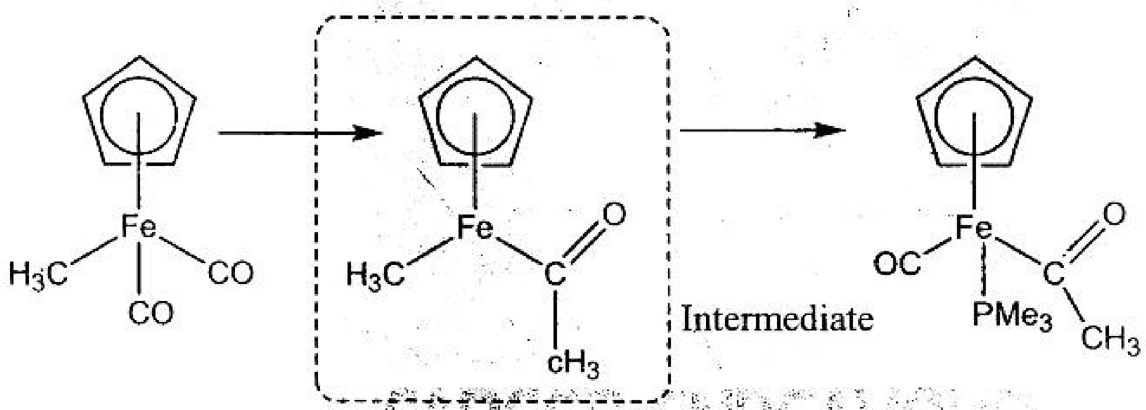
[W(η^5-C_5H_5)(μ-Cl)(CO)$_2$]$_2$

TVE(A)= (6+5+3+4)×2=36

B = nx18-A = 2×18-36=0

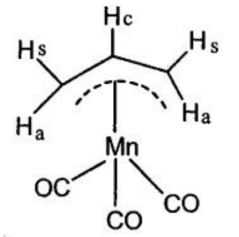
Hence, number of M-M= B/2=0/2 =0

86. Correct option is (b)



Example of migratory insertion reaction in which alkyl group insert to CO. A new ligand create acycl a vaccancy is created which is occupied by new ligand.

87. Correct option is (c)



H_c = central proton

H_a= is anti with respect to Hc

H_s= syn with respect to Hc

H_a , H_s , H_c environment are different new intensity ratio 2: 2 :1. When allyl is non-fluxional.

88. Correct option is (b)

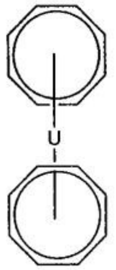
$C_2B_5H_7$ C ≡ BH

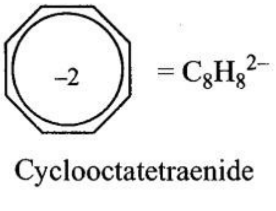
$(BH)_2 B_5H_7 \equiv B_7H_9 \equiv (B_7H_7)^{-2}$, (closo)

$(B_nH_n{}^{-2})$

89. Correct option is (a)

Structure of Uranocene





Hence, oxidation state of U=+4

Thus in uranocene U is in +4 oxidation state and have cyclooctatetraenide ligand.

90. Correct option is (a)

$[V (Co)_6]^- \rightarrow [V(CO)_6]$ (in presence of **H_3PO_4**)

$[Co(CO)_4]^- \rightarrow [HCo(CO)_4]$ (in presence of **H_3PO_4**)

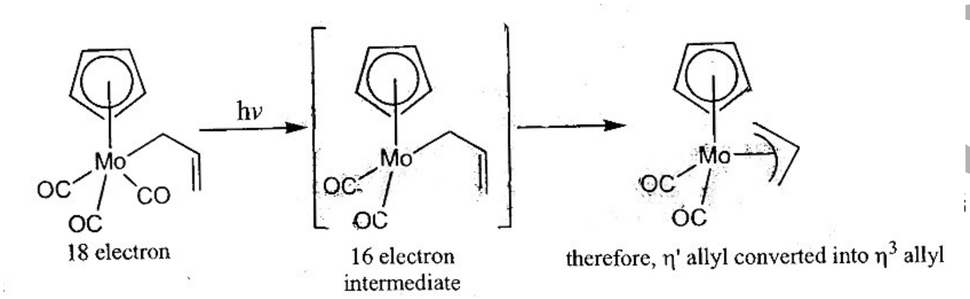
91. Correct option is (d)

Number of electron involving in metal cluster = T.V.E - 12

T.V.E in Ru(CO)$_3$ = 8 + 6 = 14 (T.V.E = total valence electron)

Hence, number of electron provided for cluster bonding = 14-12=2

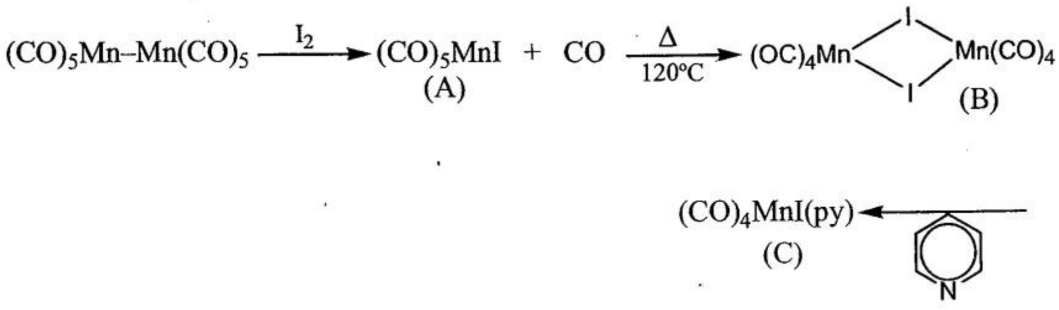
92. Correct option is (d)



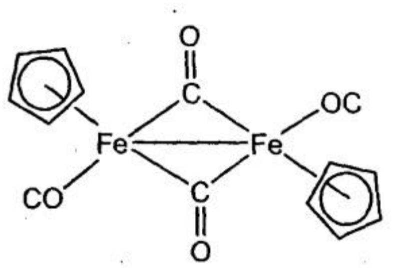
On photolysis of Z first a 16 electron intermediate is formed which is option B, and for final product allyl attains maximum heptacity therefore **η^1** allyl is converted **η^3** allyl which is option D

93. Correct option is (a)

Mechanism



94. Correct option is (a)



Terminal CO=2120-1850 **cm^{-1}**

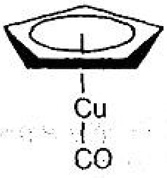
μ^2 CO=1850-1750 **cm^{-1}**

In this complex M-M bond order = 1 and two types of CO's terminal as well as ^{2}-bridging. So, **ν_{co}** band lies in both range.

95. Correct option is (d)

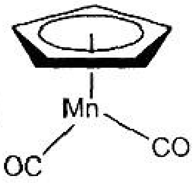
Explanation:

(A)



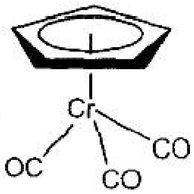
TVE = 5 + 11 + 2 = 18 electron

(B)



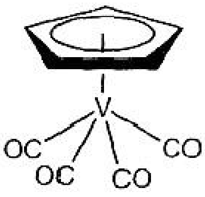
TVE = 5 + 7 + 4 = 16 electron

(C)



TVE = 5 + 6 + 6 = 17 electron

(D)

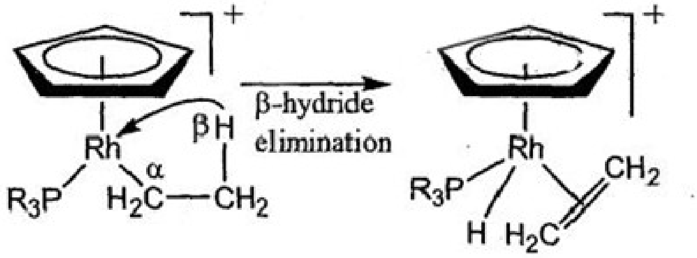


TVE = 5 + 5 + 8 = 18 electron

96. Correct option is (c)

POINT

Explanation



97. Correct option is (d)

B-H= 4e$^-$ fragment isolobal fragment should have 14 electron.

Cp + Co=5+9=14 e$^-$

98. Correct option is (b)

TVE= $(9\times2)+(8\times2)+(2\times11)+(4\times2)$

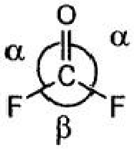
TVE = 18+ 16+ 22+8 = 64 = A

B = (n ×18) –A = (4×18) – 64 = 72-64 =8

Number of metal-metal bond = B/2=8/2 = 4

99. Correct option is (c)

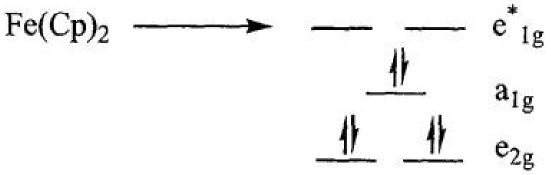
Structure of COF_2 =

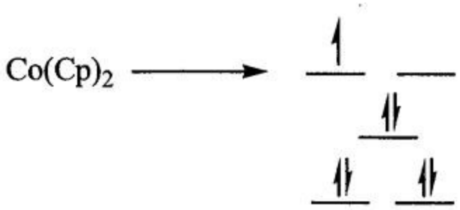


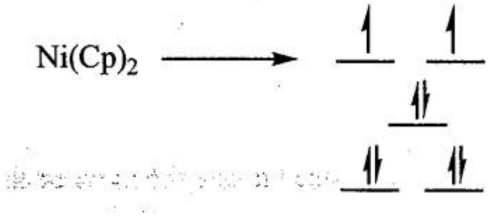
due to more space requirement for double bond the bond angle ∠F-C-O will be higher that of ∠F-C-F and also C-O bond order is larger than C-F hence, C-O bond length will be smaller than C-F.

100. Correct option is (b)

As the electron goes to e^*_{1g} (d_{xz} , d_{yz}), orbital of metallocene bond length increases as they are anologous e_g set orbital of an octahedral complex



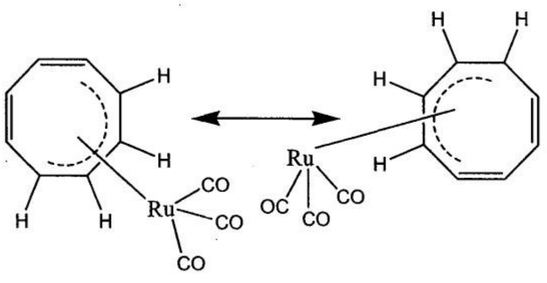




Thus, in $Ni(Cp)_2$ there are highest number of electrons in e^*_{1g} . Hence, it has highest M-C bond length.

$Ni(Cp)_2 > Co(Cp)_2 > Fe(Cp)_2$

101. Correct option is (c)



Therefore, total protons 8, but in **η^4**-mode COT attached to the four carbon and 4 protons show different environment at -140°C because fluxonial behaviour slow down and hence , 4 signals will be observed.

102. Correct option is (b)

$C_2B_3H_5 = (B\text{-}H)_2B_3H_5 = B_5H_7$

Each B-H unit give 2 electron. For cage bonding.

Hence, 5(B-H)= 5x2= 10 electron. Each hydrogen one electron,

Hence, 2H=2x1= 2 electron

Total =12 electrons

$C_2B_4H_6 = (BH)_2B_4H_6 = B_6H_8$

6(B-H) 6x2=12e$^-$

2H= 2x1=2e$^-$

Total = 14 electron

B_5H_9

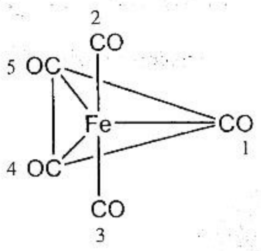
5(B-H)=5x2=10

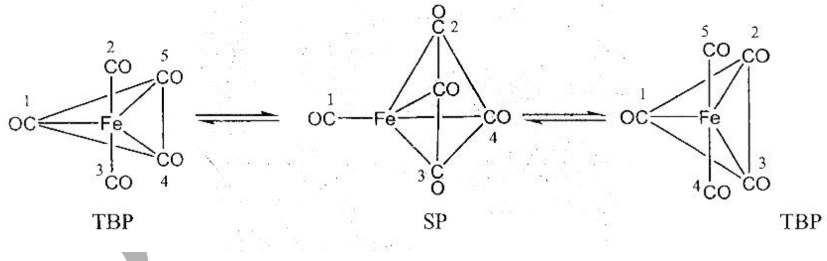
4H = 4x1= 4

Total =14 e$^-$

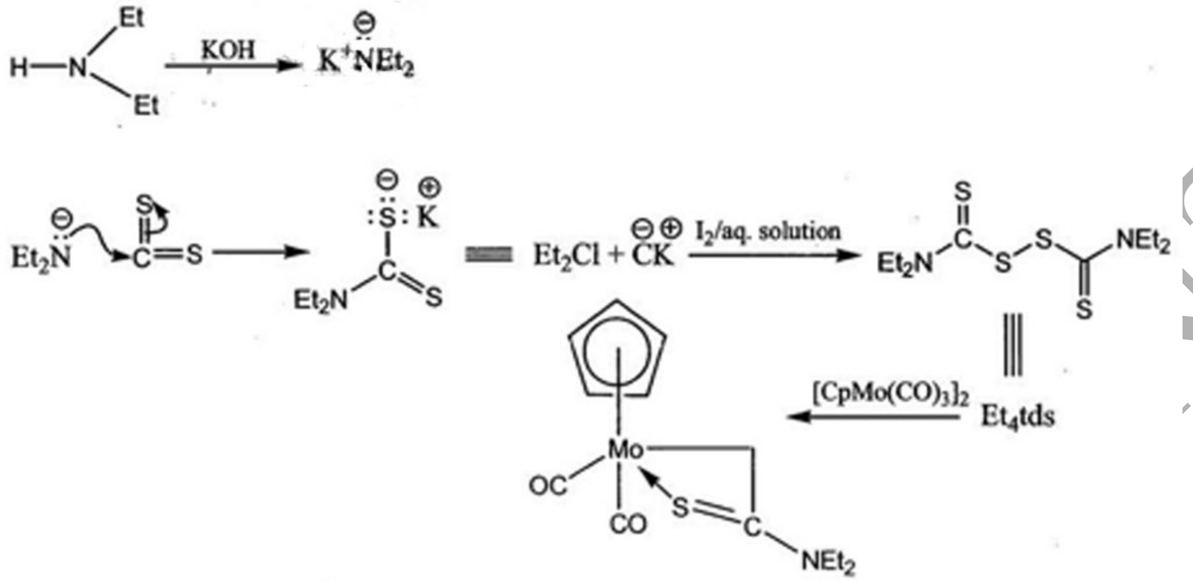
103. Correct option is (a)

During fluxional axial ligands are exchanged with equatorial ligand. Hence,

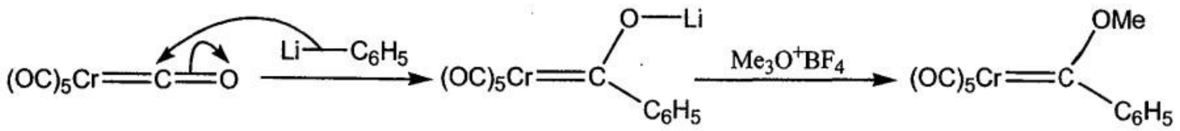




104. Correct option is (a)



105. Correct option is (a)



106. Correct option is (c)

TVE = 10+12+12=34= A.

B= (n×18) -A

B=(2×18)-34 = 36-34=2

Number of metal-metal bond =2/2=1

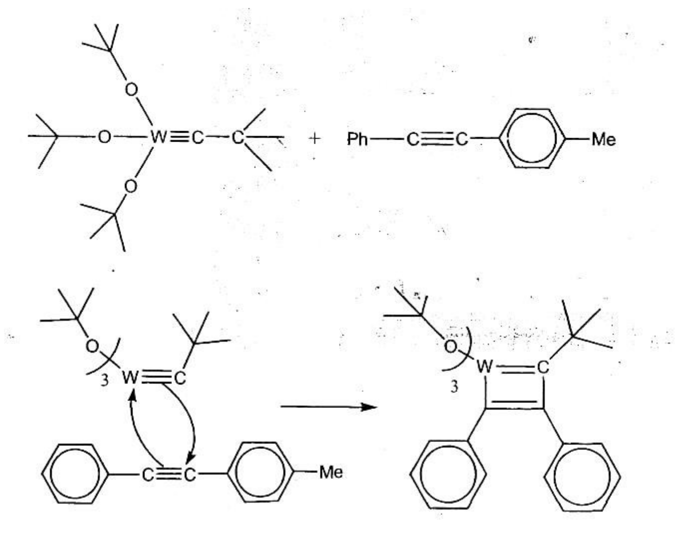
On heating :

TVE 10+12+8 = 30 =A

B=(n×18)-A= 36-30=6

Number of metal-metal bond = B/2=6/2 =3

107. Correct option is (b)

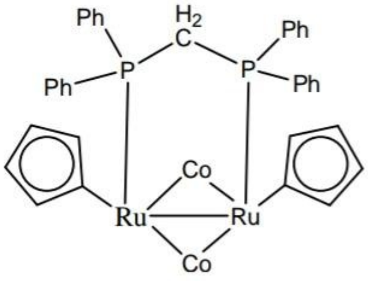


108. Correct option is (c)

T.V.E. = 8 x 2 + 5 x 2 +2 x 2 + 4= 34 = A

B = (nx18)-A=36-34= 2

Number of M-M bonds=B/2=2/2=1



3-bridging, 1-M-M bonds.

109. Correct option is (a)

When the norbornene is strained molecule because the hybridization is sp^2 when the metal attached with norbornene back-bonding takes place and due to this back-bonding the hybridization changes to sp^2-sp^3 and hence relief to strain

110. Correct option is (b)

Statement I →**$[Rh(CO)_2 I_2]^-$**

Converts CH-I and CO into CH_3COI

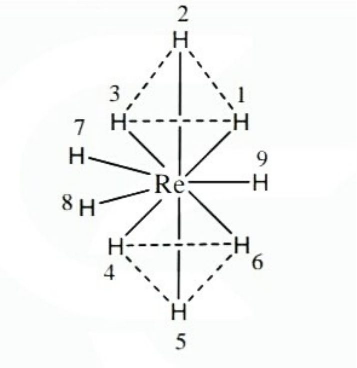
Statement → **$[Rh(CO)_2 I_2]^-$** is diamagnetic in nature.

I and II are correct but II is not correct explanation of I.

Correct explanation: Monsanto process occurs via oxidative reaction, migratory insertion and re ductive elimination reaction for that the starting compound must be square planar.

111. Correct option is (a) & (c)

$[ReH_9]^{-2}$ → Tricapped trigonal prismatic



Atoms 1 to 6 are the prism atoms, 7 to 9 are H-atom are equatorial hydrogen.

112. Correct option is (b)

$Co(CO)_3$

9+6 =15 (for 18 electron require 3 electron)

P ↔ BH_2

5 3+2 = 5 (for 8 electron require 3 electron)

CH ↔ BH_2 (for 8 electron require 3 electron)

4+1=5 3+2=5

$Ni(\eta^5- C_5H_5)$ (for 18 electron require 3 electron)

10+5=15

$Co(CO)_3 \leftrightarrow P \leftrightarrow CH \leftrightarrow Ni(\eta^5- C_5H_5)$

113. Correct option is (b)

$[Co(\eta^5- C_5H_5)B_4H_8]$

$Co(\eta^5- C_5H_5) \leftrightarrow BH$

14 4

$[BHB_4H_8] = [B_5H_5]^{-4} = [B_nH_n]^{-4} \rightarrow$ nido

$[Mn(\eta^2\text{-}B_3H_8)(CO)_4]$

$[Mn(CO)_4] \leftrightarrow [BH_2]$

7+8=15 5

$[B_3H_8BH_2] = [B_4H_{10}] = [B_4H_4]^{-6} = [B_nH_n]^{-6} \rightarrow$ Arachno

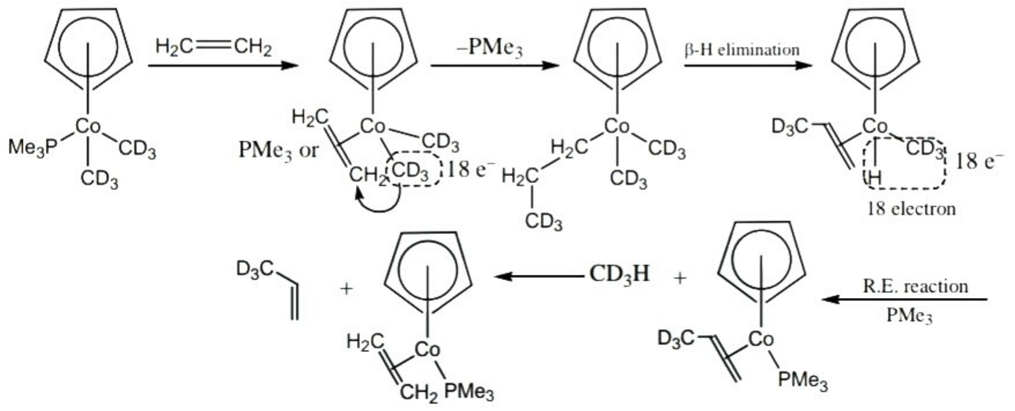
114. Correct option is (c)

$[Rh_6C(CO)_{15}]^{-2}$

TVE = 9x6 + 4 + 15x2 +2 =54+4+2+30 = 90

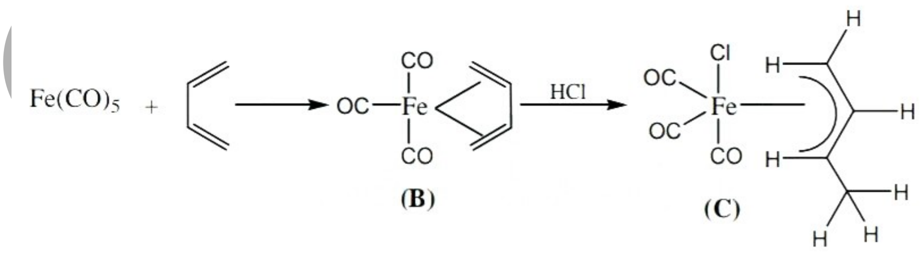
Hence, it has trigonal prism geometry.

115. Correct option is (c)



116. Correct option is (b)

Compound (C) shows four ^1H NMR signal



117. Correct option is (b)

POINT

The species having same number of electrons are called **isoelectronic.**

A =$[V(CO)_6]$=5+12=17e^-

B =$[Cu(\eta^5$- $C_5H_5)(CO)$]=11+5+2=18e^-

C =$[Co(CO)_4]^{-1}$ =9+8+1=18e^-

D=$[IrCl(CO)(PPh_3)_2]$ = 9+1+2+4=16e^-

Therefore B and D are isoelectronic species .

118. Correct option is (c)

Two fragments are isolobal if the number, symmetry properties, approximate energy and shape of their frontier molecular orbitals and the number of electrons in them are similar not identical but similar.

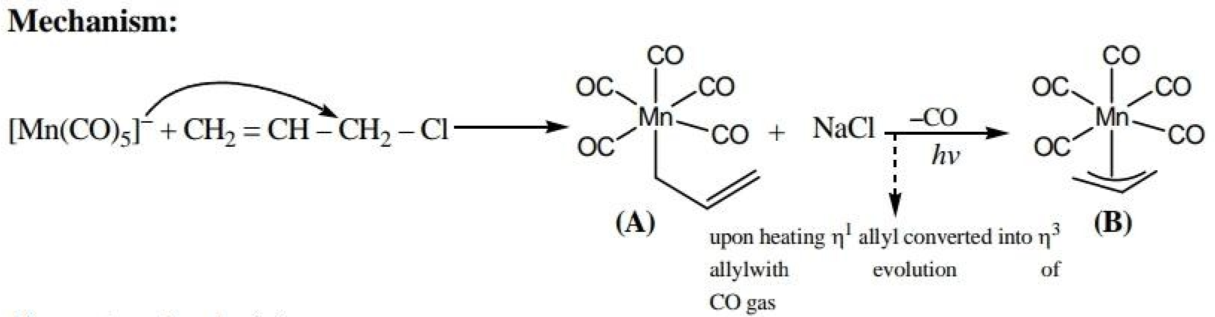
CH_3^+ = 4+3-1 = 6 ;

$[Cr(CO)_5]$=6+10=16

119. Correct option is (a)

Na $[Mn(CO)_5]$ + CH_2=CH-CH_2-Cl →

Mechanism:



upon heating η1 allyl converted into η3 allylwith evolution of CO gas

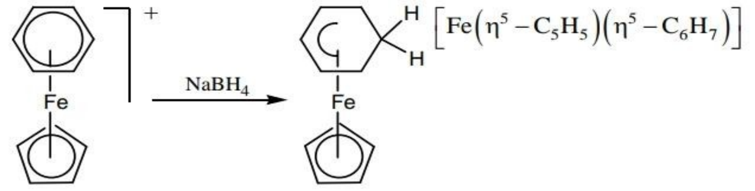
120. Correct option is (a)

$[B_6H_6]^{-2}$ has 6 + 1 = 7 bonding molecular orbital

$[B_6H_6]^{-2}$ = B-H=2x6=12 e^-

for 2 negative charge, hence 12e^- +2e^- =14e^-

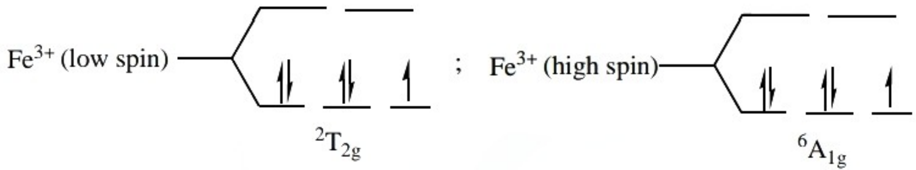
121. Correct option is (d)



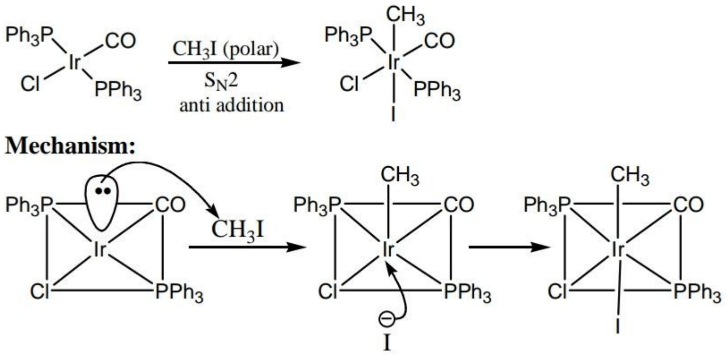
$[(\eta^5\text{-Cp})\ Fe\ (\eta^6\text{-}C_6H_6)]^+$

122. Correct option is (a)

In **$[Fe(S_2CNEt_2)_3]$,** oxidation state of Fe = +3



123. Correct option is (a)



124. Correct option is (b)

In trigonal prismatic ligand field, energy of 'd' orbital is

$\mathbf{d_{yz} = d_{xz} > d_z^2 > {}_{x^2-y^2} = d\,d_{xy}}$

Hence, the most stablized 'd' orbital is $\mathbf{d_{xy}}$

125. Correct option is (c)

Number of valence electron in CH_2 = 6

Hence, fragment having 16 electron will be isolobal to this fragment.

A→ $CpCr(CO)_2$ = 5+6+4=15

B→CpCu = 5+11=16

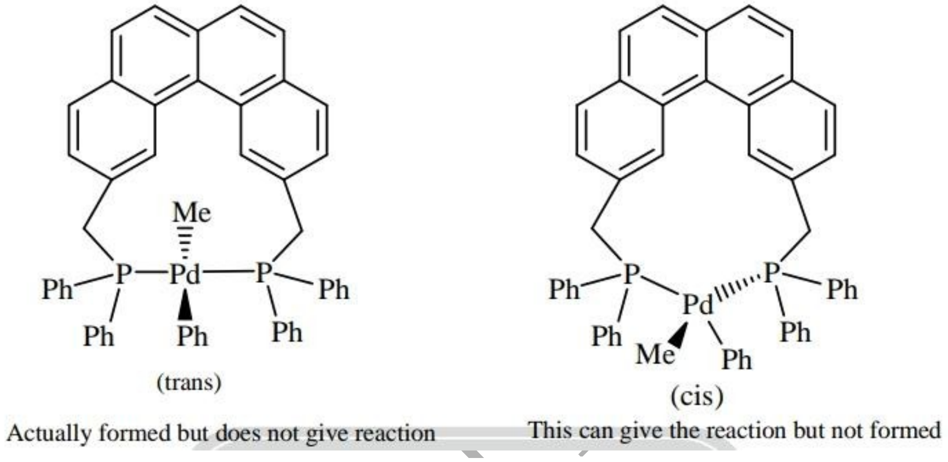
C→$Ni(CO)_2$ = 10+4=14

D→ $Cr(CO)_4$ = 6+8 = 14

E→$Fe(CO)_4$ = 8+8=16

126. Correct option is (d)

According to reductive elimination reaction mechanism cis-complex can give the product but trans-complex is not suitable for reaction and does not give reductive elimination product. Since, ligand given in option (d) forms a trans-complex with Pd(II) due to the presence of flexible methylene ($-CH_2-$) groups. Therefore, reductive elimination not occured.

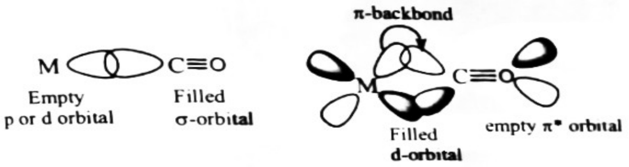

Me
Ph
P
Pd
P
Ph
Ph
Ph
Ph
(trans)
Actually formed but does not give reaction
Ph
P
Pd
P
Ph
Ph
Me
Ph
Ph
(cis)
This can give the reaction but not formed

Actually formed but does not give reaction This can give reaction but not formed

127. Correct option is (b)

Sn_9^{-4} = 9×4+4=40 , thus it follow 4n+4. Hence, it has nido structure

128. Correct option is (b)



$$\text{back bonding (synergic bonding)} \propto \frac{1}{\nu_{CO}\,(\text{streching frequency})} \propto \text{C – O bond length}$$

Compound	$[V(CO)_6]^-$	$Cr(CO)_6$	$[Mn(CO)_6]^+$	$H_3B\cdot CO$
$\nu_{C-O}\,(cm^{-1})$	1860	2000	2098	2164

$$\xrightarrow[\text{Order of } \nu_{CO} \text{ streching frequency}]{[V(CO)_6]^- < Cr(CO)_6 < [Mn(CO)_6]^+ < H_3B{-}CO}$$

$$\xrightarrow[\text{Order of C–O bond length}]{[V(CO)_6]^- > Cr(CO)_6 > [Mn(CO)_6]^+ > H_3B{-}CO}$$

Compound	$[V(CO)_6]^-$	$[Cr(CO)_6]$	$[Mn(CO)_6]^+$	$H_3B.CO$
$\bar{\upsilon}_{co}$ - cm^{-1}	1860	2000	2098	2164

$[V(CO)_6]^- < [Cr(CO)_6] < [Mn(CO)_6]^+ < H_3B.CO$

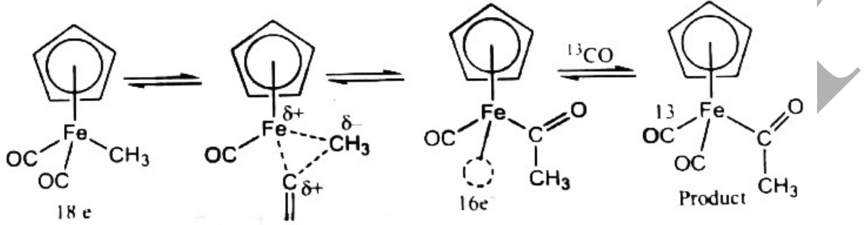
$\xrightarrow{\bar{\upsilon}_{co}\quad \text{streching}\quad \text{frequency}}$

$[V(CO)_6]^- > [Cr(CO)_6] > [Mn(CO)_6]^+ > H_3B.CO$

$\xrightarrow{\text{C-O}\quad \text{bond}\quad \text{length}}$

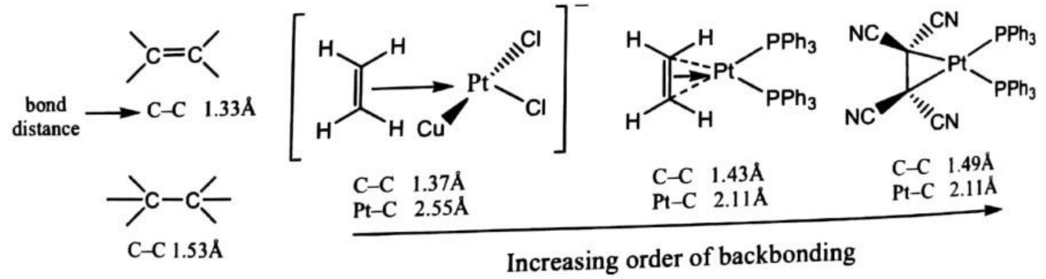
129. Correct option is (d)

The insertion of carbon monoxide into a metal carbon bond to form an acyl group is the basis of carbonylation reaction.



Intermediate

130. Correct option is (d)



Donation of π-electron of the C=C to an empty σ orbital of the metal accompanied by back donation from a filled metal d π orbital into an empty C=C π* orbital

(Synergic bonding ∝ C-C bond length)

131. Correct option is (d)

(A) $[\{Co(\eta^5\text{-}C_5H_5)\}_2(C_2B_6H_8)]$

$[\{Co(\eta^5\text{-}C_5H_5)\}_2] \rightarrow 18+10=28$ is isolobal with (B_7H_7)

$[(BH)_7\,(BH)_2\,B_6H_8]$

$B_{15}H_{17} \rightarrow B_{15}H_{15}^{-2} \rightarrow$ closo

(B) $[B_4C_2H_8] \rightarrow [(BH)_2B_4H_8] \rightarrow B_6H_{10}$ or $B_6H_6^{-4} \rightarrow$nido

(C) $[B_{10}H_{13}\,\{(Au(PPh_3))\}]$

$Au(PPh_3) \rightarrow 11+2=13$ is isolobal with B_3H_4

$[B_{13}H_{17}] \rightarrow B_{13}H_{13}^{-4} \rightarrow$nido

(D) $[C_2B_8H_{10}] \rightarrow (BH)_2B_8H_{10} \rightarrow B_{10}H_{12} \rightarrow B_{10}H_{10}^{-2} \rightarrow$ closo

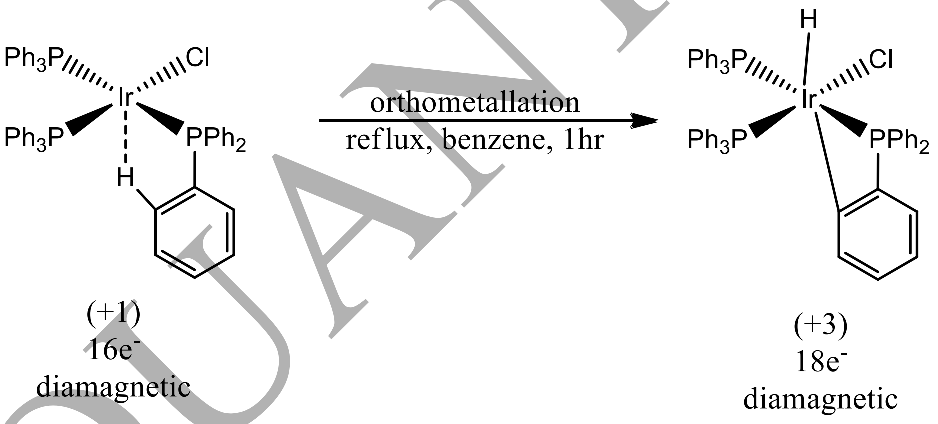
132. Correct option is (b)

$[Pd(PPh_3)_4]$ and $Ni(CO)_4$ compounds are isoelectronic (follow 18 electron rule) and isotructural in natural (tetrahedral structure)

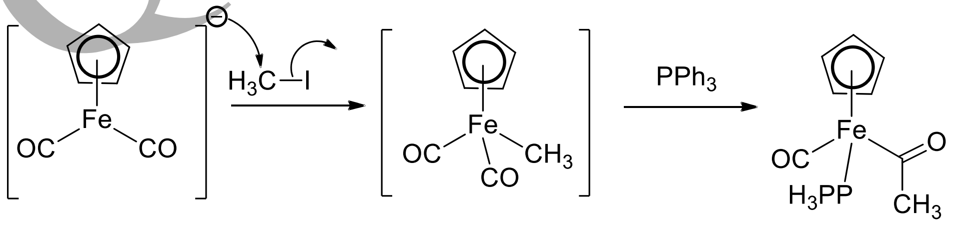
$[Pd(PPh_3)_4] = 10+8=18e^-$

$[Ni(CO)_4] = 10+8=18e^-$

133. Correct option is (b)



134. Correct option is (b)



18 e^- (A) (18e^-) (B) (18e^-)

Two signals with 3:5 intensity ratio

three signal with 3:5:15 intensity ratio

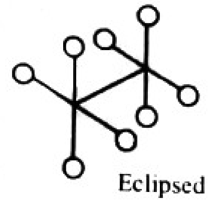
135. Correct option is (d)

$[ReCl_8]^{-2}$ =2Re^{+3} (d^4) + 8Cl^-

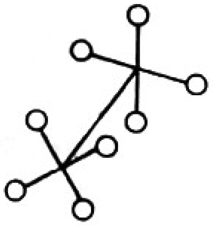
δ -bond: Eclipsed geometry

$[Os_2\ Cl_8]^{-2}$ has Os^{+3} d^5

Bond order =3: staggered



Eclipsed



Staggered

136. Correct option is (d)

In Wacker process, a Co catalyst $CuCl_2$ which could re-oxidise Pd(0) back to Pd(II)

$[PdCl_4]^{-2} + C_2H_4 + H_2O \rightarrow CH_3CHO + Pd + 2HCl + 2Cl^-$

$Pd + 2CuCl_2 + 2Cl^- \rightarrow [PdCl_4]^{-2} + 2CuCl$

$2CuCl + ½\ O_2 + 2HCl \rightarrow\rightarrow 2CuCl_2 + H_2O$

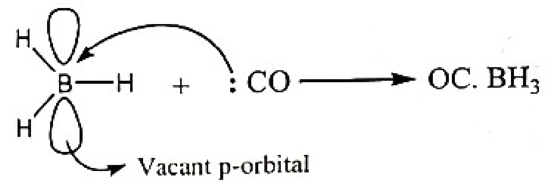
$C_2H_4 + 1/2\ O_2 \rightarrow CH_3CHO$

137. Correct option is (b)

As the electronegativity of X in PX_3 increases, π-acceptor tendency increases.

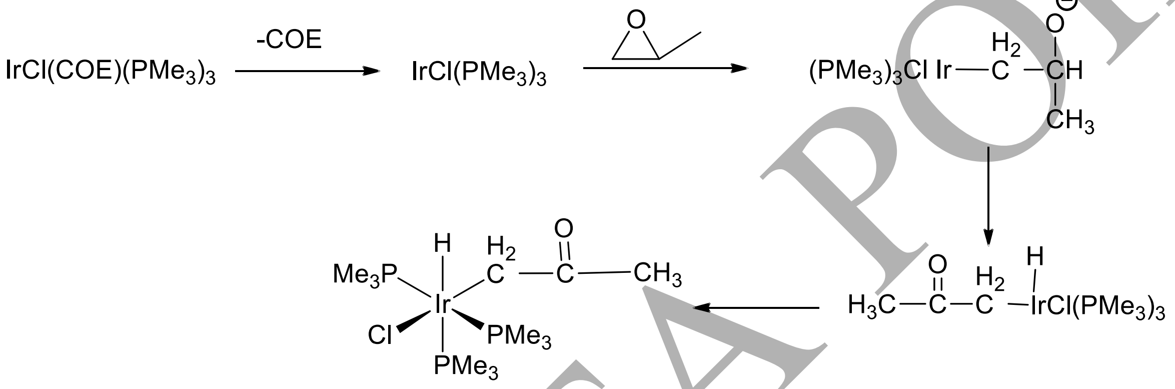
$PF_3 > P(OPh)_3 > PPh_3 > PMe_3$

138. Correct option is (b)



In BH_3.CO formation CO interact with vacant p-orbital, whereas electron is donated by antibonding orbital of CO due to which bond order increases and ν_{CO} increases.

139. Correct option is (b)



140. Correct option is (b)

Complex:

$Mo(PF_3)_3(CO)_3$ →2055, 2090

$Mo\{P(OMe_3)_3\}(CO)_3$ →1888, 1977

$Mo(PPh_3)_3(CO)_3$ →1835, 1934

$Mo(pyridine)_3(CO)_3$→ 1746, 1888

π-acceptor tendency of spectator ligand is $PF_3 > POMe_3 > PPh_3 >$ Pyridine. Therefore, PF_3 reduce more electron density from the metal in complex to pyridine consequently. As the electron density on metal decreases, M-C bond strength decreases, C-O bond strength increases. Hence, v_{CO} increases,

141. Correct option is (b)

$V_{CN} = [Fe(CN)_6]^{-3} > [Fe(CN)_6]^{-4}$

$Vco=[Cr(CO)_6] > [Cr(CO)_3(NH_3)_3]$

142. Correct option is (c)

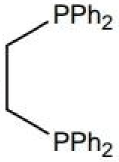
$[Rh_9P(CO)_{21}]^{-2}$ → TEC = 9×9+5+2×21+2=130

PEC=130 - 9×12=22

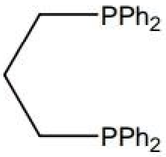
PEC/2 = 22/2 =11→ 9+2=(n+2)=nido

143. Correct option is (c)

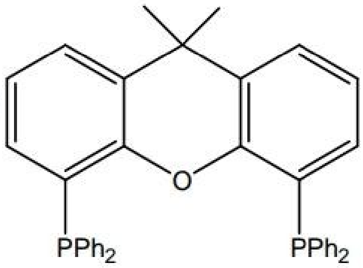
(a)



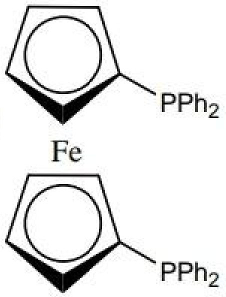
(b)



(c)



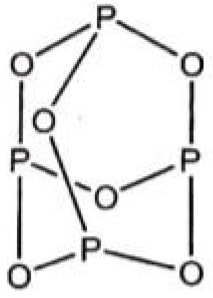
(d)



Bite angle 85^0 91^0 $>120^0$ 96^0

The linear and branched formylated product is depends upon natural bite angle of biphosphines. As the natural bite angle increases selectivity for linear product increases.

144. Correct option is (a)



145. Correct option is (a)

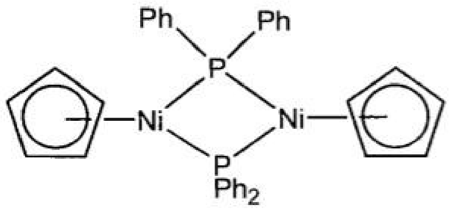
Ni = 10

Cp= $5e^-$

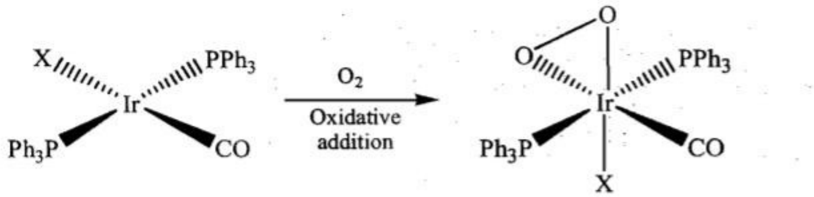
$Ph_2P=3e^-$

TOTAL = 18e

Therefore, No M-M bonds



146. Correct option is (d)



Electron withdrawing group present on the metal decreases the electron density and hence decreases the rate of oxidative addition because the rate of oxidative addition is directly proportional to the electron density on the metal.

X =	F	Cl	Br	I
Rate ($M^{-1}s^{-1}$)	1.48×10^{-2}	3.4×10^{-2}	7.4×10^{-2}	0.34

147. Correct option is (d)

Fe(-1)→ d^9 system

d^9 $ML_3 \overset{0}{\leftrightarrow}$ CH

For d^9 –ML_3, original co-ordination number will be considered as ML_6.

Therefore, **$[Fe(CO)_2(PPh_3)]^-$** having three co-ordination number, missing three from original ML_6 and similarly for CH, three ligands also missing from original CH_4 . Hence, **$[Fe(CO)_2(PPh_3)]^-$** is isolobal with CH but not with CH_2^+ ($5e^-$) because two ligands missing from original CH_4.

148. Correct option is (d)

$[Ru_6C(CO)_{17}]$

TEC = 8x6+4+17×2=86

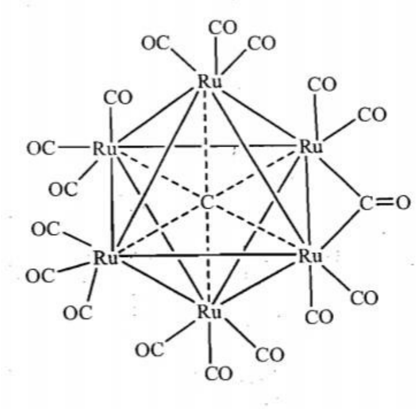
PEC= TEC- n x 12.

PEC= 86- 6x12

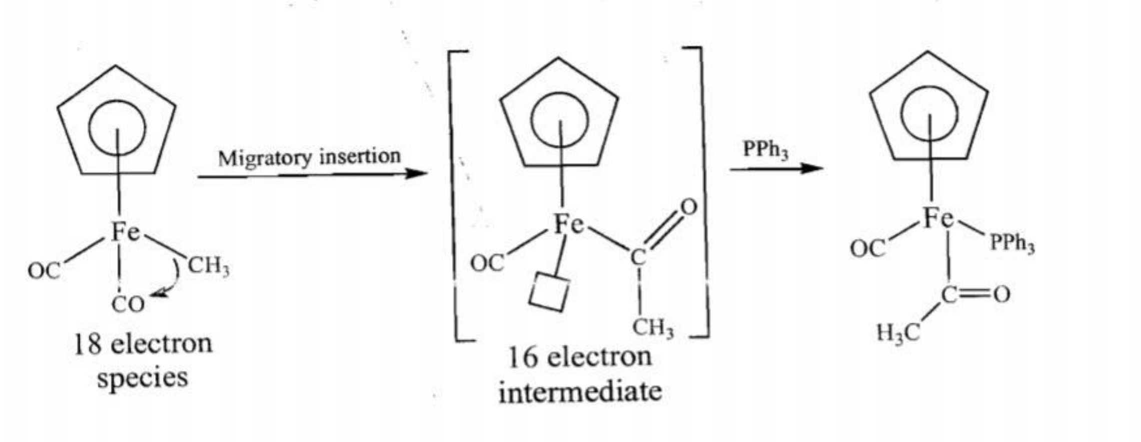
PEC= 86 - 72=14

PEC/2 = 14/2=7 (n+1) => Closo

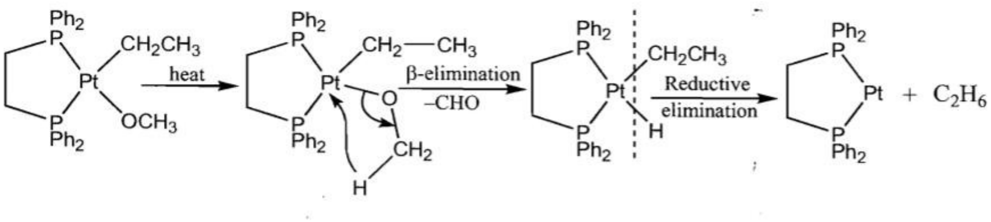
In the cluster **[$Ru_6C(CO)_{17}$]**the carbon atom is encapsulated at cavity of cluster and equally interacted with all Ru centres.



149. Correct option is (c)

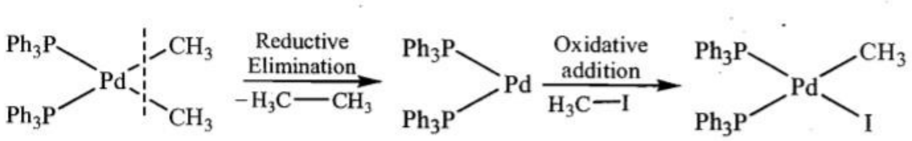


150. Correct option is (c)

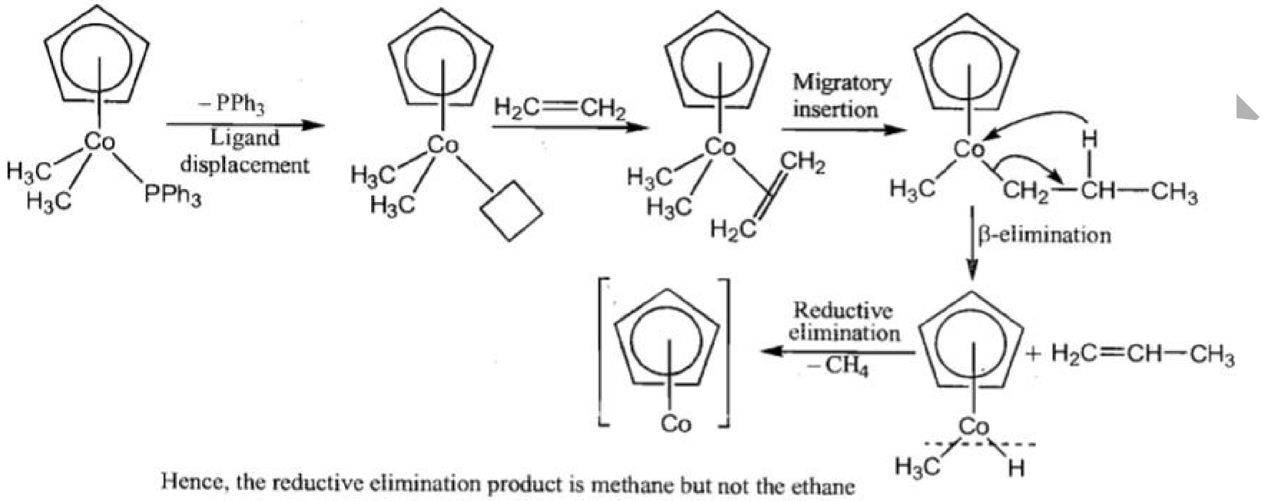


For reaction A:

For Reaction B:

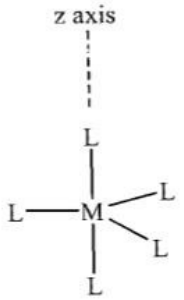


For reaction C:



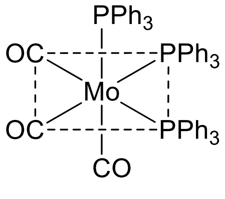
Hence, the reductive elimination product is methane but not the ethane

151. Correct option is (b)

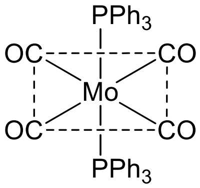


Two ligands are present on z-axis therefore, **d_{z^2}** -orbital is involved in σ bonding. Also three ligands are present in xy plane, therefore, **$d_{x^2-y^2}$ and d_{xy}** orbitals are involved in σ -bonding. Thus the **$d_{x^2-y^2}$ and d_{xy}** orbitals remain nonbonding.

152. Correct option is (c)



fac-isomer



trans-isomer

The number of CO bands in fac-[Mo $(PPh_3)_3(CO)_3$] =2

The number of CO bands in trans-[Mo$(PPh_3)_2(CO)_4$]= 1

153. Correct option is (b)

In aqueous medium, the most stable vanadium species is hydrated vanadyl ion $[VO]^{+2}$ i.e

$[VO(H_2O)_5]^{+2}$

154. Correct option is (d)

Cp_2Fe

$10e^- + 8e^- = 18\ e^-$

Number of electron in anti-bonding orbital = 0

Cp_2Co

$10e^- + 9e^- = 19e^-$

Number of electron in anti-bonding orbital = 1

Cp_2Ni

$10e^- + 10e^- = 20e^-$

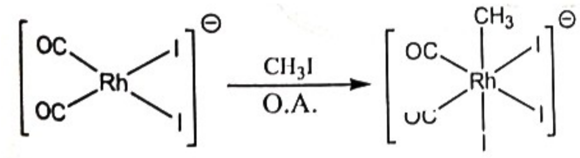
Number of electron in anti-bonding orbital = 2

As the number of electron present in the anti-bonding orbital increases , M-ligand bond becomes weak and hence, bond length increases. Therefore, the correct order of M-C distance is

$Cp_2Ni > Cp_2Co > Cp_2Fe$

155. Correct option is (a)

This step is the slowest step and hence rate determining step.



156. Correct option is (b)

$[Fe_5(CO)_{14}N]^-$

TEC= (8x5) + (14×2)+5+1 = 40+28+6 =74

PEC =74-(12x5)=14

PEC/2= 14/2 =7 ie.n+2

Thus, it is a nido cluster.

$[Co_6(CO)_{13}N]^-$

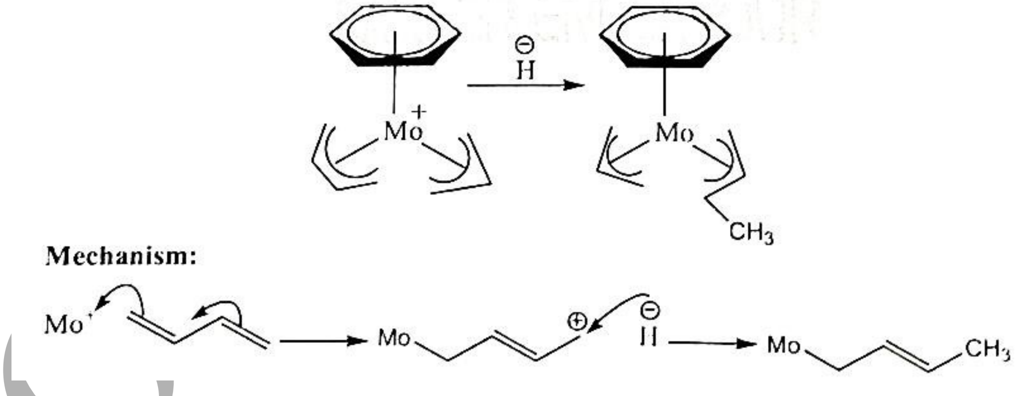
TEC= (9x6) + (13x2)+5+1 = 54+26+6 = 86

PEC=86 - (6x12) = 14

PEC/2=14/2 = 7 i.e n+1

Thus, it is a closo cluster.

157. As per DMG rule , the rate of nucleophilic addition is :



158. Correct option is (a)

Square planar complexes undergo associative pathway. So, ligand substitution process can be better understood in terms of crystal field activation energy (CFAE). Considering trigonal bipyramid or square pyramidal geometry in Transition state (T.S.), C.F.A.E. can be calculated.

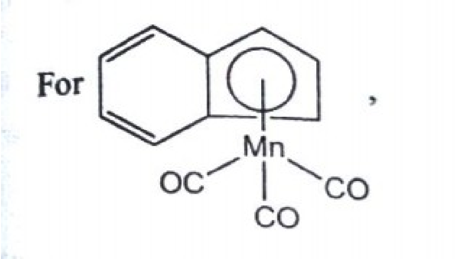
C.F.A.E. (Dq) = C.F.S.E. (Dq) of T.S - C.F.S.E. (Dq) of square planar complex.

The Dq value increases of the heavier congeners and it makes heavier congeners more inert. So rate of substitution will be

Ni(II)> Pd(II)> Pt(II)

159. Correct option is (d)

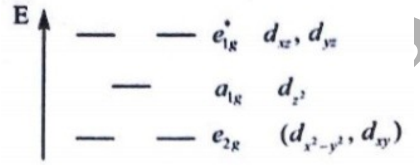
The highest rate of substitution of a CO ligand on heating with PPh_3 is easy where slippage of haptacity is easy.

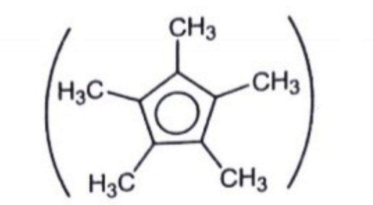


slippage is easy because it is not at the cost of aromatic character ($\eta^5 \rightarrow \eta^3$).

But $\eta^5 - Cp^*$, complexes, rate decreases because with respect Cp slippage of haptacity is due to at the cost of aromatic character.

160. Correct option is (b)

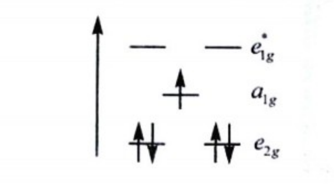




Due to high field strength of Cp* , it forms low spin complexe and having one unpaired electron

$Cp_2^*Mn = 2Cp^* = 10e^-$ and $Mn = 7e^- = 17e^-$

12e electrons are in the lower orbitals and remaining five electrons occupies the orbital as follows.



Electronic Configuration = $e_{2g}^4\ a_{1g}^1$

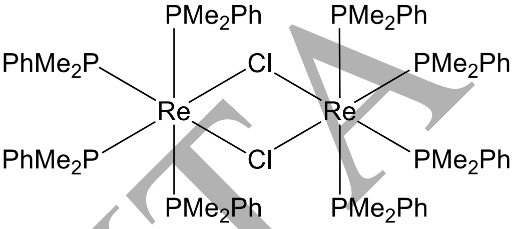
161. Correct option is (c)

Taking 18 valence electron as guide, the products will be predicted.

$[Mo(N_2)_2(PMe_2Ph)_4] \xrightarrow{\Delta} [(\eta^6\text{-}PhPMe_2)Mo(PMe_2Ph)_3] + N_2$

18 V.E 18 V.E

$[ReCl(N_2)(PMe_2Ph)_4] \xrightarrow{\Delta}$



$+ N_2$

18 V.E 18 V.E 18 V.E

(Cl as a bridging ligand)

162. Correct option is (c)

$[Fe_4C(CO)_{12}]^{-2}$

Polyhedron electron count = T.E.C.-12 x n = [4 x 8 + 4 + 24 + 2] -12x4 = 62 – 48 = 14

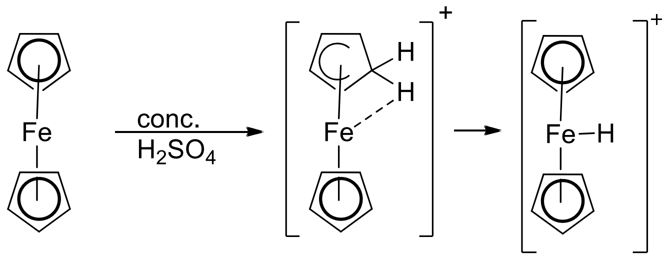
Hence, x= PEC/2 = 14/2 = 7 = n+3 i.e arachno

T.E.C.= 62

So, it adapts the butterfly structure expected for arachno

163. Correct option is (c)

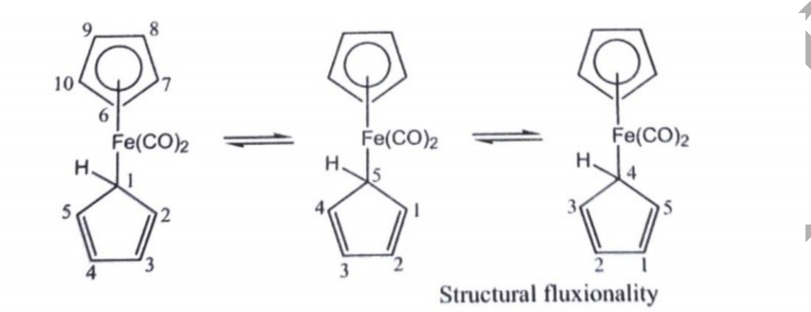
Mechanism



Protonation of ferrocene with strong acids results intermediate through exo-attack

164. Correct option is (a)

At +30°C , the compound shows structural fluxionality.



Structural fluxionality

So, the two Cp rings display the different bonding modes σ(η^1) and π (η^5).

At room temperature (30°C) observed doublet due to η^5-Cp and η^1-Cp

but at -80°C, four peaks observed.

5 : 2 : 2 : 1

↓ ↓ ↓ ↓

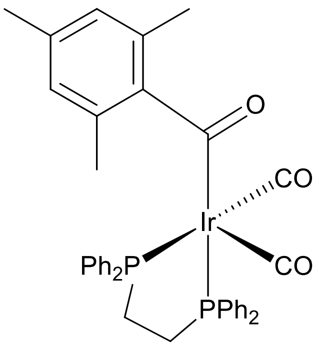
H_{6-10} H_{2-3} H_{4-5} H_1

165. Correct option is (d)

The product (A) shows three strong bands at 1986, 1935 and 1601 cm^{-1}.

Three different IR bands suggest, the different CO environment in the complex.

For compound



three different -C≡O environments are present.

Terminal -C≡O , $\bar{\upsilon}_{\text{-C}\equiv\text{O}}$ (terminal) →2120-1850 cm and M-C(=O)-CH_3 $\bar{\upsilon}_{\text{-CO}}$ =1700-1600 cm^{-1}

compound (b) and compound (c) show two and four different C≡O environments.

166. Correct option (b)
In bent mode NO donates one electron to metal centre, thus statement A is incorrect.
IR range for bent NO is $1525 - 1690\ cm^{\text{FW}}$ whereas for linear NO it is $1690 - 1900\ cm^{\text{FW}}$. Thus statement B is correct.

Electronic configuration for CO is,

Electronic configuration for NO is,
Thus statement C is also correct.

167. Correct option (c)
Statement A is correct, as in order to form pi bond between metal and carbine, 2 electrons are donated.
Statement B is incorrect, the given carbene is Fischer carbene and it is electrophilic in nature.
Statement C is correct, rotation around the Cr=c(OME)Me double bond has low barrier.

168. Correct option (d)
TVE for $[Ru_{\{}(CO)_{\text{W}\sim}B]^{\text{F}}$ is 86
TVE for $[Os_{\{}(CO)_{\text{WV}}P]^{\text{F}}$ is 90
TVE for $[Os_{,}(CO)_{\text{W\{}}]$ is 64

Following the below table,

S.No	Total Valence Electrons	Cluster Framework
1	64	Square
2	86	Octahedral
3	90	Trigonal Prismatic

169. Correct option (b)

In option (b) both Fe follows 18e rule.

Fe = 8e

Cp = 5e

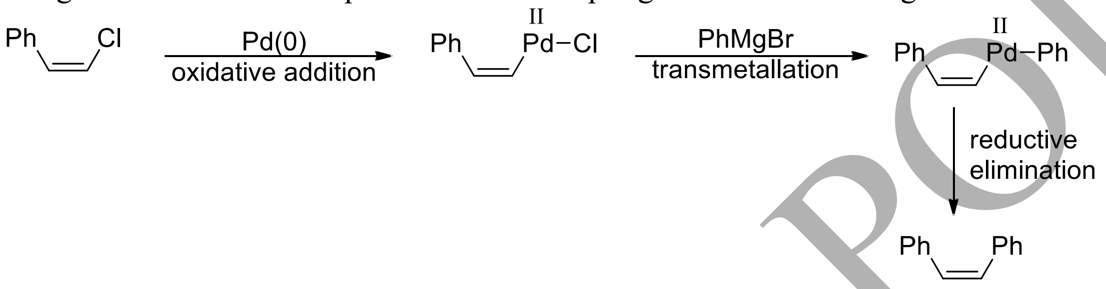
Linear NO = 3

Bridging CO = 2

Total 18e, hence, thermodynamically stable.

170. Correct option (b)

The given reaction is example of Kumada coupling between Pd and Mg



171. Correct option (b)

Carbene whether it is singlet or triplet, they are bent in configuration.

In the presence of +M groups (which is chlorine here), the carbine will be singlet.

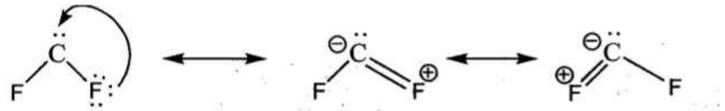
3

Main Group Elements

Hints & Solutions

1. Correct answer (b):

Stabilisation via back-bonding. Due to innert pair effect stability of +2 oxidation state increases down the group.



2. Correct answer: (a)

Alkali metals in liq. NH_3 ,act as source of electrons and are supposed to be a good one-electron reducing agents.

$$M + (x+y)\,NH_3 \rightarrow \left[M\left(NH_3\right)x\right]^{+} + \left[e^{-}\left(HN_3\right)y\right].$$

These solvated electrons can reduce O2 molecule to superoxide ion.

$$\left[e^{-}\left(NH_3\right)y\right] + O_2 \rightarrow O_2^{-} + yNH_3$$

These superoxide ions can combine with solvated metal ion to give alkali metal superoxides.

$$\left[M\left(NH_3\right)x\right]^{+} + O_2^{-} \rightarrow MO_2 + xNH_3$$

3. Correct answer: (a)

Compounds	**Uses**
(A) Na_3PO_4	Water softener
(B) Ar_3PO_4	Plasticizers
(C) Et_3PO_4	Insecticides

(D) $CaHPO_4.2H_2O$	Toothpaste

4. Correct

answer: (a)

$B_2O_3 + 3H_2O \rightarrow 2H_3BO_3$ (orthoboric acid)
$N_2O_5 + 3H_2O \rightarrow 2HNO_3$ (nitric acid)
$SO_3 + 3H_2O \rightarrow H_2SO_4$ (sulfuric acid)
$P_4O_{10} + 6H_2O \rightarrow 2H_3PO_4$ (orthophosphoric acid)

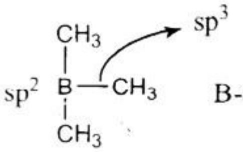
5. Correct option (a)

Correct answer is (a) **closo-{B_nH_n}** species has always -2 charge.

6. Correct answer is (a)

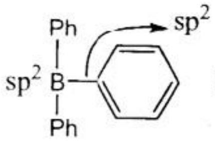
BCl→ pπ→-pπ back bonding

$B(CH_3)_3$



B-attracts B–CH_3 electron (Hyperconjugation).

BPh_3



B and C both are sp^2-hybridised. No shifting of electrons (Resonance).

$BCl_3 > BPh_3 > BMe_3$

Correct answer is (a)

7. Correct answer is (b)

(A) IE, for O and S are 1314 and 1000 kJ mol^{-1} difference 1314-1000=314
(B) For N and P IE, are 1402 and 1012 kJ mol^{-1} difference 1402-1012=390
(C) For P and As IE, are 1012 and 947 kJ mol^{-1} difference 1012-947 = 165 (less 300 kJ)
(D) Also for IE, difference is less than kJ mol^{-1}

8. Correct answer is (b)

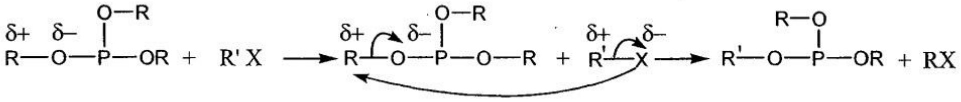
456 789

$Na \xrightarrow{\quad\quad\quad} Na^+(NH_3)_x + e^-(NH_3)_y$
$NH_4^+ Br^- + e^-(NH_3)_y \rightarrow NH_3 + 1/2H_2 + yNH_3 + Br^-$
$Na^+(NH_3)_x + Br^- \rightarrow NaBr + xNH_3$

9. Correct answer is (d)

$(SN)_x$ because it is a giant cross linked molecule and have mobile electrons.

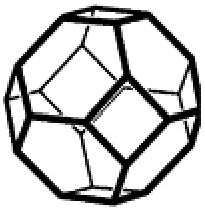
10. Correct answer is (a)

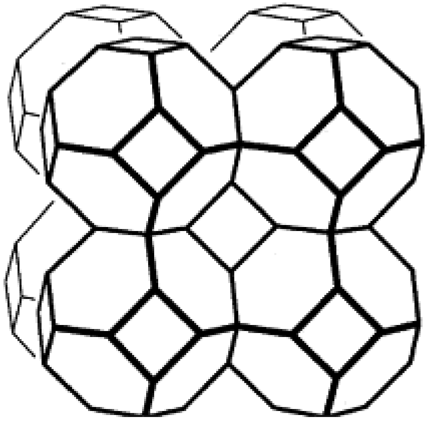


Because P-O bond very strong affinity very high not easily break. So, R-O bond break.

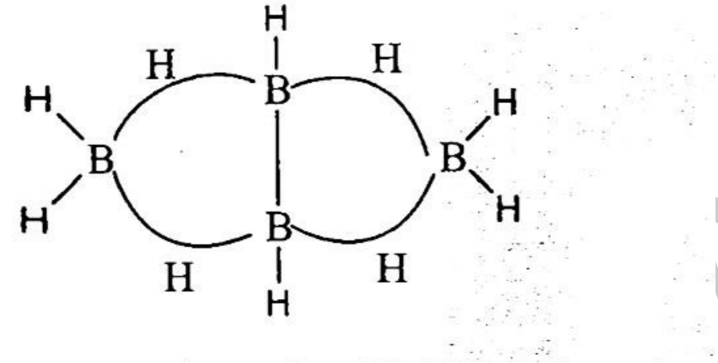
11. Correct answer is (c)

The structure of Sodalite cage zeolites is a truncated octahedral (as shown below)





12. Correct answer is (c)



s = number of B–H–B bonds = 4

t = number of B-B-B = 0

y =number of B-B bonds = 1

x = number of BH_2 groups + twice the BH_3 groups = 2

Therefore, styx code = 4012

13. Correct option (b)

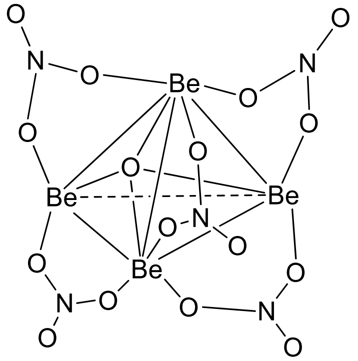
The Reaction mechanism of typical Bayer's process is given below

$Na_2B_4O_7 + 16Na + 8H_2 + 7SiO_2 \rightarrow 4NaBH_4 + 7Na_2SiO_3$

This is used for synthesis of $NaBH_4$ from borax

14. Correct answer is (a).

The correct structure of beryllium nitrate contains Be cluster with 5 NO3 units and one O as a part of cluster. (as shown below)

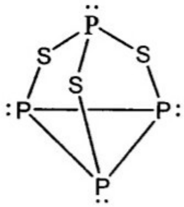


15. Correct answer is (d).
Smaller the internuclear distance between two atoms, stronger will be the bonds. The increasing inter nuclear distance is as Cl-O < S-O < P-O< Si-O .Therefore strength of p**π**-d**π** bonding is Cl-O> S-O> P-O >Si-O.

16. Correct answer is (c).
$NCl_3 + 4H_2O \rightarrow NH_4OH + 3HOCl$
$PCl_3 + 3H_2O \rightarrow$, $H_3PO_3 + 3HCl$ (two different Acids) ,
$AsCl_3 + 3H_2O \rightarrow H_3AsO_3 + 3H_2$ (two different acids)

17. Correct answer is (b).
Alumino silicate is the most used catalyst in oil industry; mostly it is used for the process of Cracking.

18. Correct answer is (a).



19. Correct answer is (d).
Low oxidation state complexes are air sensitive as they easily lose electrons to oxygen, but they are not water sensitive as they do not bind to a π–donor molecule like H_2O.

20. Correct answer is (d)
$PbCl_2$ and $PbSO_4$ are ionic compounds and insoluble in cold water. Therefore, cannot be used for deposition of Pb and Pb(Et) is toxic.

21. Correct answer is (b)
Among these elements K is least electronegative and F is most electronegative. Therefore electronegativity difference is highest for the pair K, F**.**

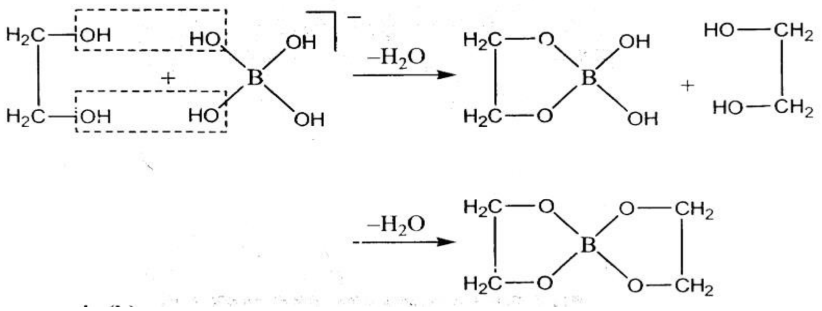
22. Correct answer is (b)
$C_2B_4H_8$

$(BH)_2B_4H_8 = B_6H_{10} \longrightarrow [B_6H_6]^{-4} \rightarrow$ nido borane

23. Correct answer is (b).

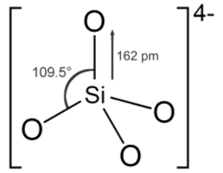
$B(OH)_3 + OH^- \leftrightarrow [B(OH)_4]^-$ (reversible reaction)

In presence of ethylene glycol, $B(OH)_4^-$ is consumed as shown below and boric acid behaves as strong acid.

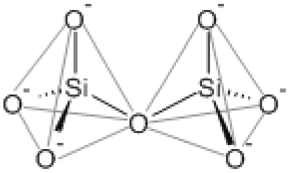


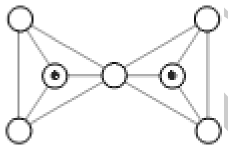
24. Correct answer is (d)

Neso silicates (or Ortho or Island silicates) are the simplest silicates which contain discrete SiO_4^{4-} tetrahedral unit

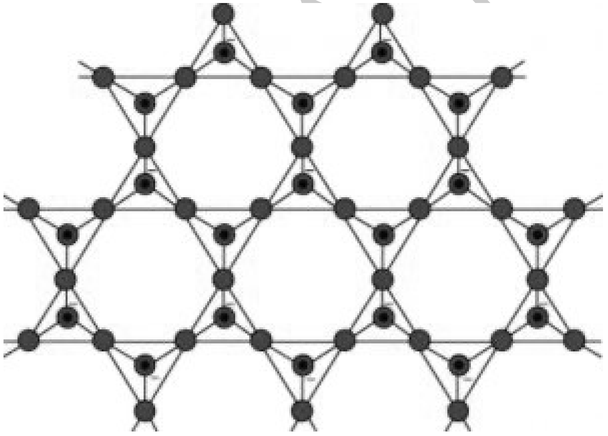


Soro silicate (or Pyro silicate or disilicate) contain $Si_2O_7^{6-}$ ions which are formed by joining two tetrahedral SiO_4^{4-} which share one oxygen atom at one corner (one oxygen is removed while joining).

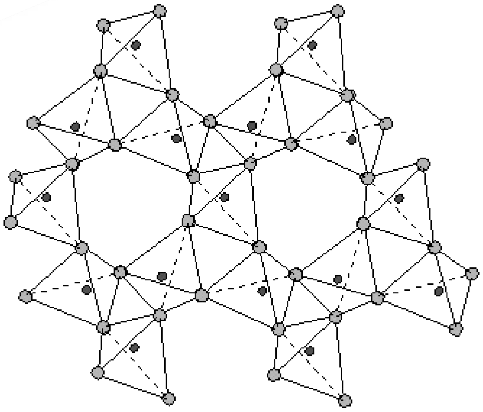




Phyllo or two dimensional (2-D) silicates is $(Si_2O_5)_n^{2n-}$. Each SiO_4 tetrahedron shares three oxygen atoms with others and thus by forming two-dimensional sheets.



Tecto or three dimensional (3-D) or Framework silicates is $(SiO_2)_n$. All the oxygen atoms of SiO_4 are shared with other tetrahedra and thus by forming three-dimensional network.



25. Correct answer is (d)

As we go down the group in periodic table for sodium family, the number of electrons increases and their attraction towards nucleus increases and simultaneously with addition of new energy shells but increase in distance is more pronounced as that of increase in e^- , So Na loses e^-s very easily therefore lowest ionization energy .

In the case of inert gas family, Ne has its complete octet, strongly connected with nucleus e attraction and do not give e^- s to lose easily therefore highest ionization energy.

Thus Na, Ne pair have highest difference in their first ionization energy in given option.

26. Correct answer is (a)

Nitrous acid (N_2O) which is commonly known as laughing gas used as a propellent in whipping cream. So, also known as whippits or nangs**.**

27. Correct answer is (c)

The Flame proof fabrics contain urea and phosphoric acid $H_2NC(O)NH_2.H_3PO_4$

28. Correct answer is (c)

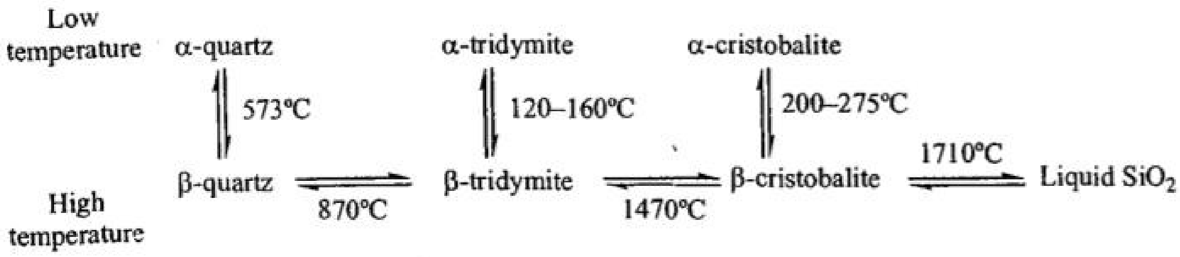
(A) **N_2O_3 :** $HNO_2 + HNO_2 \rightarrow N_2O_3 + H_2O$

(B) **N_2O_4**: $HNO_3 + HNO_2 \rightarrow N_2O_4 + H_2O$

29. Correct answer is (a)

As we move from Nb-Ta and Mo-W there is introduction of electron into f-orbital. As the shielding power of f-orbital is very less. Therefore, as we move from La-Lu in 4f series the size decreases, this is termed as Lanthanide contraction. This leads to slight increase in size of 5d metal than 4d. Due to this size of d and 5d metals are nearly similar. Hence Nb-Ta and Mo-W have similar covalent radii.

30. Correct answer is (b)



31. Correct answer is (d)

$FeCl_3.6H_2O + SOCl_2 \rightarrow FeCl_3 (s) + SO_2(g) + HCl(g)$

32. Correct answer is (c)

Large difference between the sizes of Li and Cs. So, it is difficult to get a solid solution of these two metals.

33. Correct answer is (c)

$ClF_3 + SbF_5 \rightarrow [ClF_2]^+ [SbF_6]^-$

SbF_5 is a very strong F- acceptor and leads to the formation of ionic compound.

34. Correct answer is (d)

Bond order=3 , bond order is directly propotional to bonding energy.
High bond order and HOMO LUMO gap

35. Correct answer is (b)

Cesium iodide (CsI) in crystalline form is used as the scintillator for the detection of protons and alpha particles. Sodium iodide (NaI) containing a small amount of thallium is used as a scintillator for the detection of gamma waves and zinc sulfide (ZnS) is widely used as a detector of alpha particles.
Since in the question, it is asked about radiations (that means gamma rays) thus answer should be NaI

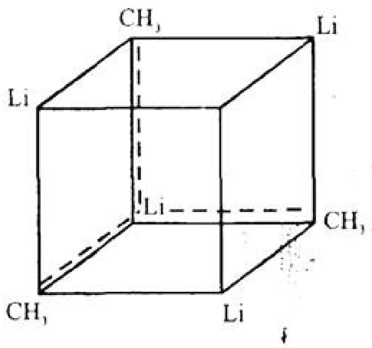
36. Correct answer is (a)

H_3PO_3 is a dibasic and reducing in nature . Thus it should contain two OH groups in the structure.

37. Correct answer is (c)

In solid state, aluminum fluorides have 3D network structure unlike Al_3Cl_3

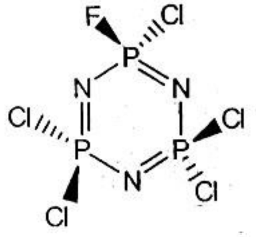
38. Correct answer is (c)

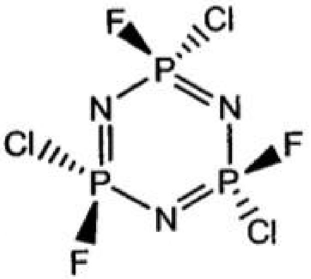


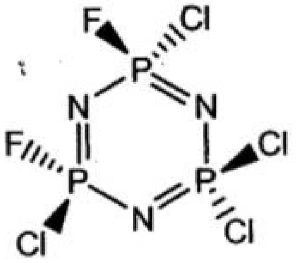
The diagram clearly indicates the four centered-two electron interaction (4c-2e). This takes place in **$Li_4(CH_3)_4$.** The sp^3 hybrid orbital is of carbon while the three s-orbitals are of three surrounding lithium atoms.

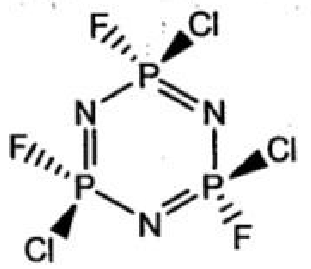
39. Correct answer is (c)

$N_3P_3Cl_3F$ (A) = only 1 isomer



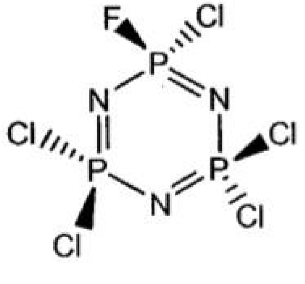


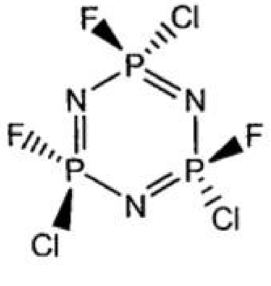


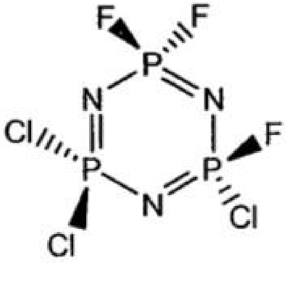


$N_3P_3Cl_4F$ (B) = 3 iso

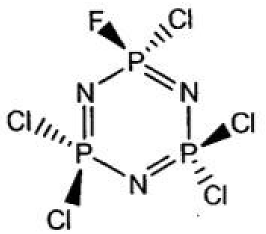
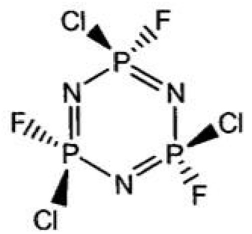
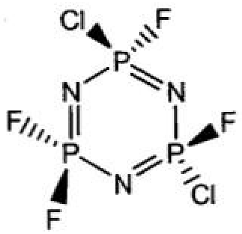
$N_3P_3Cl_3F_3$(C) = 3 isomer



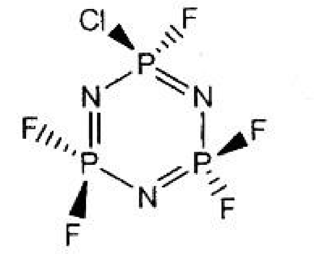




$N_3P_3Cl_2F_4$ (D) =3 isomer

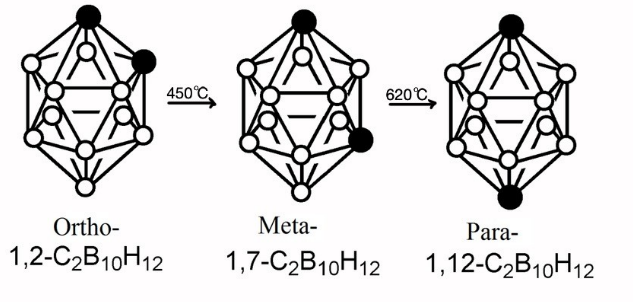
$N_3P_3ClF_5$ (E) = 1 isomer



40. Correct answer is (a)

Relative acidic strength of xenon fluorides follows order $XeF_6 > XeO_3 > F > XeOF_4 > XeF_4, XeO_2F_2 > XeF_2$. This order depends upon (i) number of lone pair (ii) number of 'F' atoms

41. Correct answer is (a)



Ortho- $1,2\text{-}C_2B_{10}H_{12}$ Meta- $1,7\text{-}C_2B_{10}H_{12}$ Para- $1,12\text{-}C_2B_{10}H_{12}$

$C_2B_{10}H_{12}$ is show three isomeric derivative which is depend on the the temperature.

42. Correct answer is (d)

Styx rule B_5H_9
$(BH)_pH_q$ $(BH)_5H_4$
S= number of BHB unit ↑ ↑
T= number of BBB unit p q
Y=number of BB unit
X= excess hydrogen attached to B alone.
Hydrogen balance
$s+x=q$ $s+x=4$
orbital balance
$t+s=p$ $t+s=5$
Electron balance
$p+q/2 = s+f+y+x$ $t+y=5-4/2=3$
$p= f+ y + q/2$

s	t	y	x
2	3	0	2
3	2	1	1
4	1	2	0

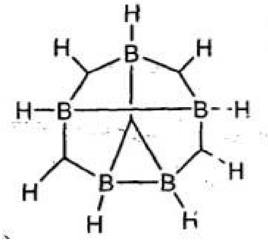
$s+x=4$

$t+s=5$

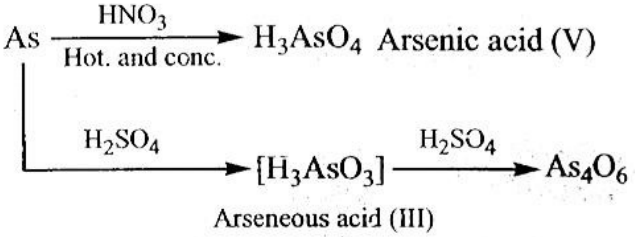
$t+y=5-\frac{4}{2}=3$

s	t	y	x
2	3	0	2
3	2	1	1

$\boxed{4}\boxed{1}\boxed{2}\boxed{0}$ → more symmetry



43. Correct answer is (d)



$$\mathrm{As}\xrightarrow[\text{Hot. and conc.}]{HNO_3}H_3AsO_4\ \text{Arsenic acid (V)}$$

$$\mathrm{As}\xrightarrow{H_2SO_4}[H_3AsO_3]\xrightarrow{H_2SO_4}As_4O_6$$

Arseneous acid (III)

The reason is that HNO_3 is better oxidising agent than H_2SO_4, also acts as dehydrating agent**.**

44. Correct answer is (a)

Chromium is extracted from chromite ore:

(I) $4FeCr_2O_4, +8Na_2CO_3 +7O_2 \rightarrow 8Na_2CrO_4 +2Fe_2O_2 +8CO_2$

(II) $2Na_2CrO_4+H_2SO_4 \rightarrow Na_2SO_4 + Na_2Cr_2O_7 + H_2O$

(III) $Na_2C_2O_7+2C \rightarrow Cr_2O_7 +Na_2CO_3 +CO$

(IV) $Cr_2O_3 +2A1 \rightarrow Al_2O_3 + 2Cr$

45. Correct answer is (b)

The electronegativities of elements are

Ca	Al	As	S
1.0	1.5	2.0	2.5

46. Correct answer is (c)

As positive charge increases the size decreases while with increase in negative charge increase the size. This is due to increase in Z_{eff}, in former case while decrease in Z_{eff}, in later case. Hence, order of size is $\mathbf{S^{2-} > S > S^{2+} > S^{4+}}$

47. Correct answer is (d)

HF exist as H_2F_2 , and it act as fluoride donar if strong fluoride acceptor is present like SbF_5, AsF_5, Therefore, the reaction will be HF 2 moles = H_2F_2

H_2F_2 (lewis base) + SbF_5 (lewis base) → $[H_2F]^{+}$+ $[SbF_6]^{-}$

SbF_5 act as Lewis acids as it has vacant 'd' orbital of suitable energy

48. Correct answer is (c)

All the ions are isoelectronic. Therefore, the size depends upon effective muclear charge.

Size of isoelectronic ions ∝ $\frac{=}{>}$

	F^-	O^{2-}	Na^+	Mg^{2+}
Atomic number	9	8	11	12
Number of electrons	10	10	10	10

Hence, the order of size will be $O^{2-} > F^- > Na^+ > Mg^{2+}$

Since, atomic number increases.

Therefore, z, increases .

Therefore, size decreases.

49. Correct answer is (c)

The reaction is as follows

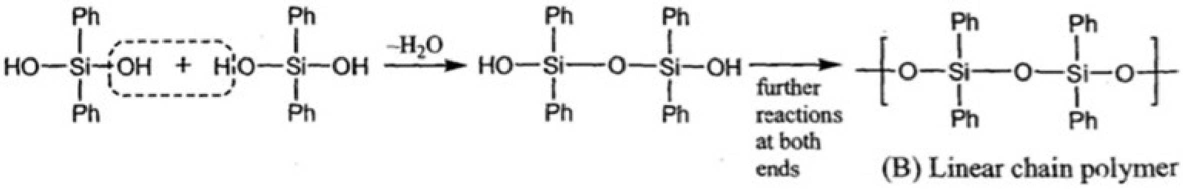
$Ph_2SiCl_2 + 2H_2O \rightarrow Ph_2Si(OH)_2 + 2HCl$

1:2 Diphenyl disilanol

Diphenyl- (A)

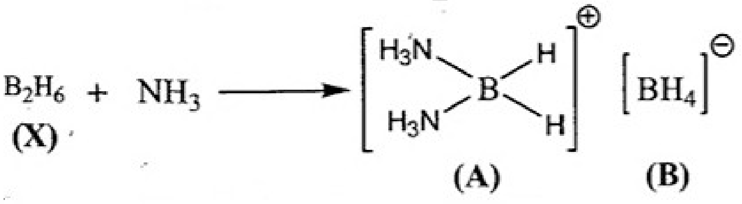
-dichloro silane

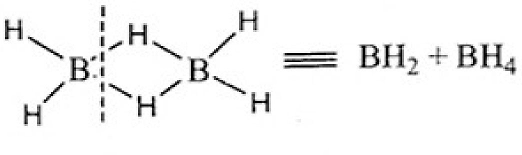
Now, (A) undergo condensation polymerisation to yield (B), which is an inorganic silicon, polymer, as follows



50. Correct answer is (a)

Diborane reacts with ammonia as





Here NH_3 show unsymmetrical cleavage.

'Y' is actually [A+B].

In 'Y' 'B' part gives quintet and 'A' part gives triplet by 'B' and 'H' coupling.

51. Correct answer is (a)

The crown ether binds metal cation in their cavity. They are selective as they have fixed ring size.

POINT

Crown ether

Crown-4	Li^+
crown-5	Na^+
crown-6	K^+
crown-7	Rb^+
crown-8	Cs^+

Therefore, 12-crown-4 is best suited for Li^+ cation. After then as the size increases binding capacity decreases.

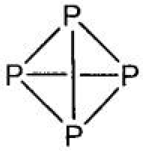
52. Correct answer is (a)

The reaction of XeF_6 with $NaNO_3$ takes place as

$XeF_6 + NaNO_3 \rightarrow XeOF_4 + NaF + NO_2F$

53. Correct option is (a)

All the allotropic phosphorous forms changes into white P, discrete units. Which has structure.



54. Correct option is (d)

Pseudo halogen are polyatomic analogous of Halogen whose chemistry resemble with true Halogen common example. **CN^-, N_3^- , SCN^-, NCN^{2-}**.These anions contain nitrogen atoms.

55. Correct option is (c)

The average of oxidation states is $\frac{;?9?;}{9} = \frac{==}{9}$

$H_5P_3O_{10}$ = +5+3x-20 =0 , 3x =+15 , x=+5

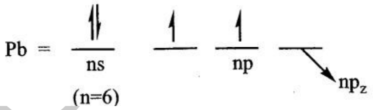
$H_5P_3O_7$ = +5+3x-14 = 0 ,x=+3

$H_5P_3O_8$ = +5+ 3x-16=0 , x=+ 11/3

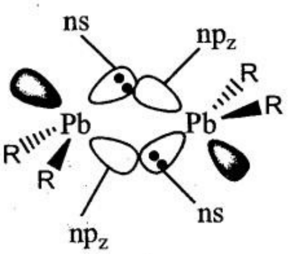
$H_5P_3O_9$ = +5+3x-18=0 , x= +13/3

56. Correct option is (a)

Due to IPE ns² electron-pair become inactive. In Pb



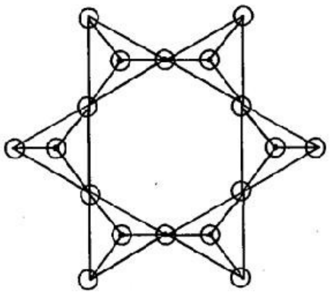
Therefore, the structure must be



57. Correct option is (a)

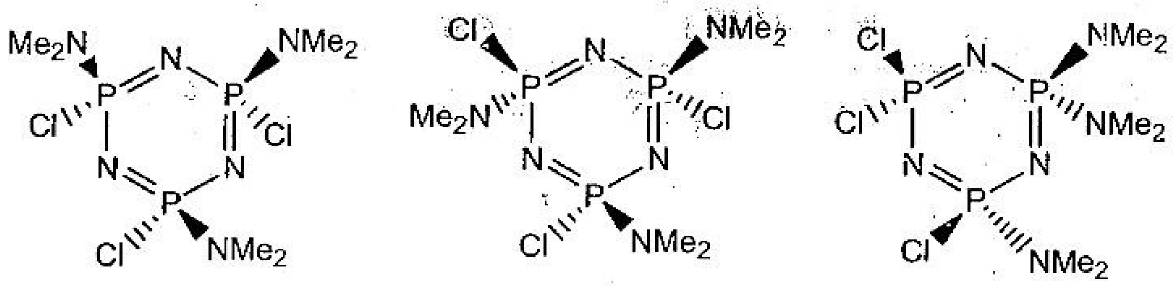
Acidic strength of Borane depends upon
(i) number of Boron atoms
(ii) decapping
Hence, the correct order of acidity is **$B_5H_9 < B_6H_{10} < B_{10}H_{14}$**

58. Correct option is (b)
The structure of $[Si_6O_{18}]^{-12}$, is

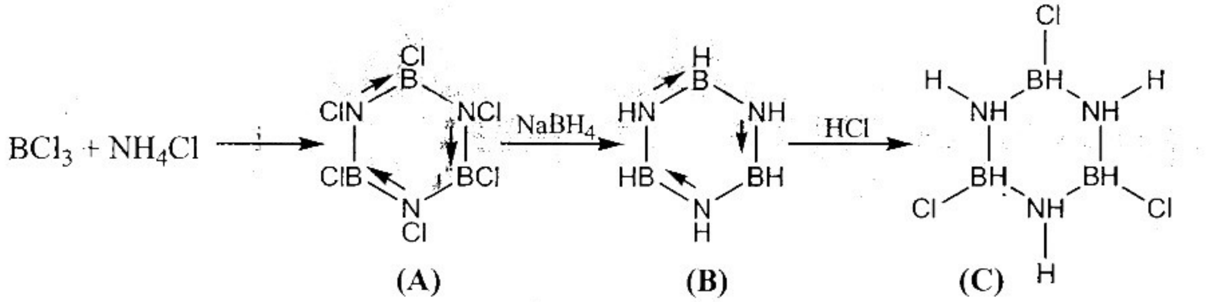


Hence, the number of linked tetrahedrals = 6
The size of ring = 12

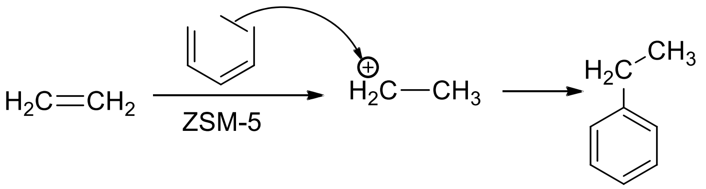
59. Correct option is (b)



60. Correct option is (a)

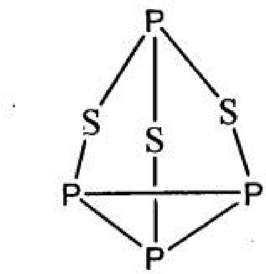


61. Correct option is (a)
ZSM-5 stands for Zeolite Socony Mobil-5, it is an alluminosillicate zeolite belonging to pentasil family of zeolite. It's chemical formula is $Na_nAl_nSi96\text{-}nO_{192}.16H_2O$. It is widely used in industries for heterogeneous catalyst for hydrocarbon isomeriasation.
The mechanism followed for the above reaction is



62. Correct option is (a)

Structure of $\mathbf{P_4S_3}$ is



Number of P-S bond=6
Number of P-P bond = 3

63. Correct option is (b)

$POCl_3 \rightarrow POCl_2^+ + Cl^-$
$POCl_6 + Cl \rightarrow POCl_4^-$
(1) $Et_3N \xrightarrow{l5q} (OPCl_2 .NEt_3)^+ + \overset{POCl3}{Cl^-}$
$POCl_6 + Cl^- \rightarrow POCl_4^-$ (Cl^- concentration is not enhanced)
(ii) $KCl \xrightarrow{l5q} K^+ + Cl^-$ POCl3
The Cl^- ion produced in this reaction increases the concentration of Cl^- and it is not consumed by $POCl_3$
(iii) $FeCl_3 + OPCl_3 \rightarrow POCl_2^+ + CeCl_4^-$
(iv) $SbCl_6 + OPCl_3 \rightarrow POCl_2^+ + SbCl_6^-$

64. Correct option is (c)

LaI_2 exists as La^{+3} ($2I^-$)(e^-)
The electron present is responsible for metallic cluster and high electrical conductivity.

65. Correct option is (d)

8C (graphite) + K^+ (am)+e^- (am) → $[K (am)]^+$ $[C8]^-$ (s)
Due to the presence of unpaired electrons in π* band of graphite it is paramagnetic and its electrical conductance increases. It has eclipsed layer structure

66. Correct option is (a)

$6S_2Cl_2 + 16NH_3 \xrightarrow{\text{CCl4, or C6H6}} S_4N_4 + S_8 + 12NH_4Cl$

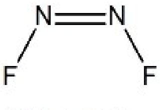
67. Correct option (a)

$B_4H_{10} + NMe_3 \rightarrow Me_3NB_3H_7 + Me_3NBH_3$

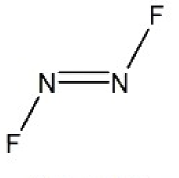
68. Correct option is (d)
K + graphite →$[\text{graphite}]^- K^+$
H_2SO_4 +graphite = $[\text{graphite}]^+ HSO_4^-$

69. Correct option is (a)
Bi_5^{+3} = 5x5-3 = 22
Hence, (4n+ 2), closo
On addition of 2 electron it become (4n+4), nido

70. Correct option is (c)
NF has two isomers,



$1C_2 + 2\sigma_v$

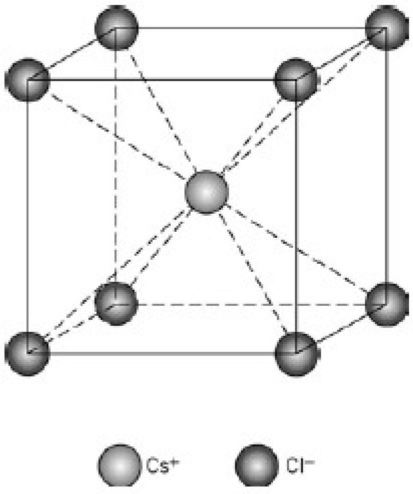


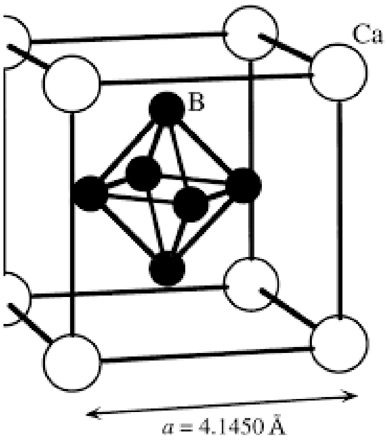
$1C_2 + 1\sigma_h$

71. Correct option is (b)
Generally, ionisation energy increases on moving from left to right in a period in periodic table.
- Ionisation energy decreases as we move down in given group
- Ionisation energy will be more for full filled and half filled orbital.

72. Correct option is (c)
$[PMo_{12}O_{40}]^{3-}$ is less basic. It is slightly less basic than ClO_4^-

73. Correct option is (a)
ollows





CaB_6 and CsCl both have BCC like structure, the B_6 cluster is present at the body center of Ca lattice.

74. Correct option is (c)
Zn → $3d^{10}\ 4s^2$

Ga→ $4s^2\ 4p^1$
Ge→ $4s^2\ 4p^2$
As→ $4s^2\ 4p^3$
Full filled and half filled orbital have higher ionization energy.
Hence, Ga have lowest first ionisation energy because removal of an electron Ga^+ achieve stable nobel gas configuration.

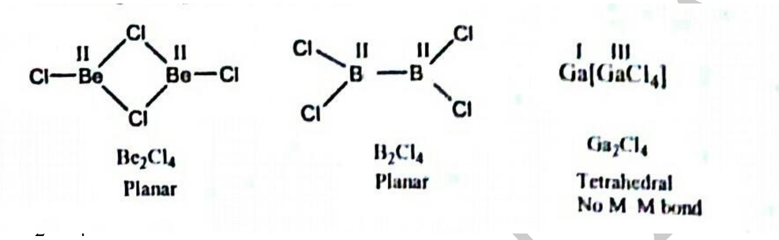
75. Correct option is (d)
The above reaction undergoes as follows

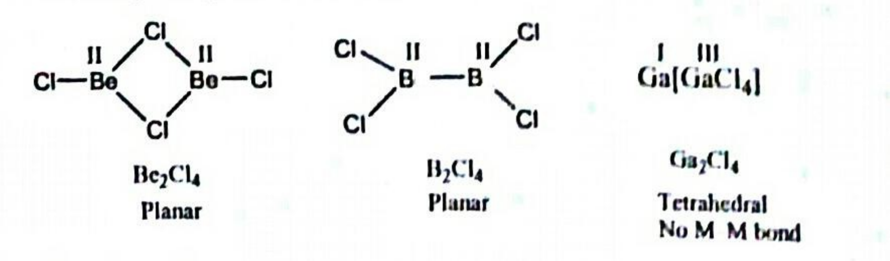
=FF°C H4IH45JK LMNOP4MQ5Q

$XeF_6 + 2NF \rightarrow Na_2[XeF_8] \dashrightarrow [XeF_6] \dashrightarrow$ Perxenate + 2NaF
(Z) (A)

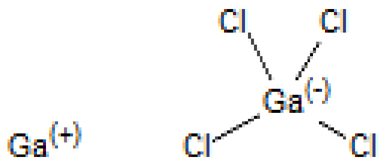
76. Correct option is (b)
On descending the group, the stability of +3 oxidation state increases and that of +5 oxidation state decreases. Size usually increases on descending the group (P = 1.10 A^0 and As = 1.21 A^0). Thus, $AsCl_5$ is thermally less stable than PCl_5 and As is larger than P but less stability of $AsCl_5$, is not due to larger size of As, instead it is due inert pair effect.

77. Correct option is (c)
Structures of **Be_2Cl_4 (I), B_2Cl_4 (II) and Ga_2Cl_4** are





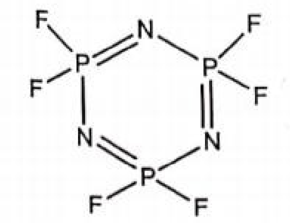
Be_2Cl_4 = Planar
$Ga^I[Ga^{III}Cl_4]$
Ga_2Cl_4 = tetrahedral , No M-M bond



78. Correct option is (a)

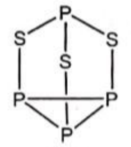
$$B_{10}H_{14} + 2Et_2S \longrightarrow B_{10}H_{12}(Et_2S)_2 \xrightarrow[-2Et_2S \atop -H_2]{HC\equiv CH} C_2B_{10}H_{12}$$

79. Correct option is (b)



N = Planar (sp^2)
P = Tetrahedral (sp^3)

80. Correct option is (c)



P_4S_3

Valence electron (N) = P = $2s^2\ 2p^1$ =5
S=$2s^2\ 2p^4$ = 6 $\xRightarrow[\text{R5SKQ}]{}$ 4×5+6×3 = 38
2c- 2e bond (x) = 9
$X = \frac{\text{Un - N}}{\text{V}} = n= \frac{\text{Vx + N}}{\text{U}} = \frac{\text{=U+ 38}}{\text{U}} = 7$

81. Correct option is (b)
The correct reaction of B_2H_6 with O_2 and water are
$B_2O_3 + H_2O \xleftarrow{O_2} B_2H_6 \xrightarrow{6H_2O} 2B(OH)_3 + H_2$

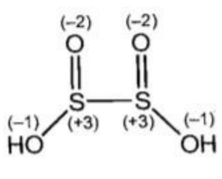
82. Correct option is (a)
Magic number →shell model of nucleus
Liquid drop model of nucleus → nuclear fission
Actinides →radioactivity
Threshold energy→ Q-value

83. Correct option is (a)
$[Al_2(OH)_2\ Si_4O_{10}] \xRightarrow[\text{by Al(III)and charge balance by K(I)}]{\text{replaced by 1/4 of Si(IV)}} KAl_2(OH)_2(Si_3AlO_{10})$

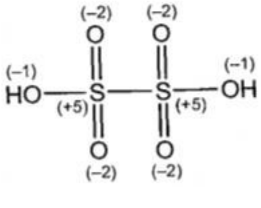
Pyrophyllite Muscovite

84. Correct option is (c)

Dithionous acid, $H_2\overset{(+3)}{S_2}O_4$

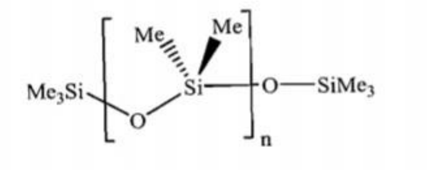


Dithionic acid, $H_2\overset{(+5)}{S_2}O_6$



85. Correct option is (b)

Poly dimethyl siloxane (PDMS) is :

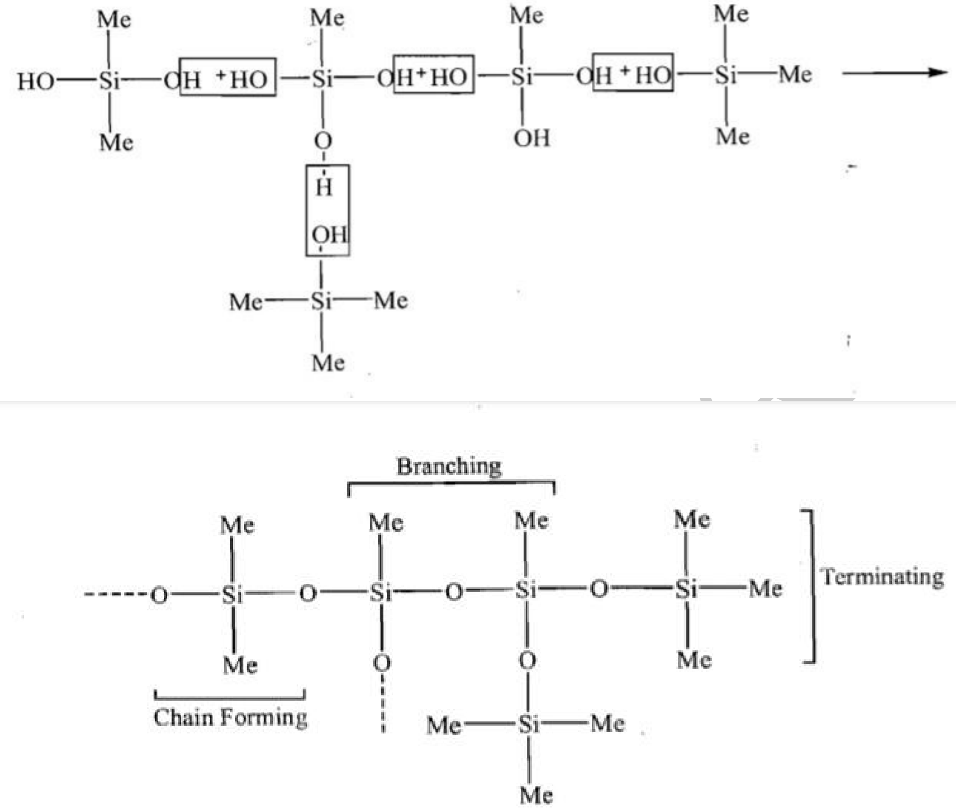


In Siloxanes

Me_3SiCl : used as terminating agents $Me_3SiCl + H_2O \rightarrow Me_3Si(OH)+HCl$

Me_2SiCl_2, used as chain forming $Me_2SiCl_2+2H_2O \rightarrow Me_2Si(OH)_2 + 2HCl$

$MeSiCl_3$: used as cross linkers for branching $MeSiCl_3+ 3H_2O \rightarrow MeSi(OH)_3 + 3HCI$



• Nuclear spin of ^{10}B =3

Nuclear spin of ^{11}B = 3/2

	B→H	C←H
Electronegitivity:	2.04 2.1	2.5 2.1

This indicates that polarities of B-H and C-H bonds are opposite

•Thermal neutron absorption cross section for ^{10}B=3837 Barn and for ^{11}B=0.005 Barn

•Boron resists attack by boiling conc. aqueous NaOH or fused NaOH upto 500°C.

$$B+ NaOH (aq) \rightarrow \text{No reaction}$$

Boron react with fused alkali to give sodium metaborate and H_2.

87. Correct option is (c)

- LiF is sparingly soluble in water but for large anions such as ClO_4^- , the Li^+ salts are soluble in water.

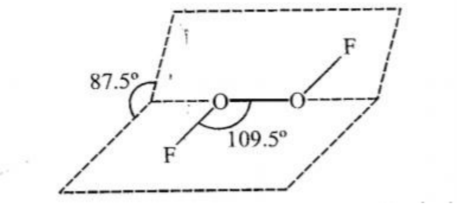
- Standard reduction potential $[E^0]$ of Li is more negative than that of Na.

$$Li^+ (aq) + e^- \rightarrow Li (s) \quad [E^0]_{red} = -3.04$$
$$Na^+ (aq) + e^- \rightarrow Na(s) \quad [E^0]_{red} = -2.71$$

- Enthalpy of hydration:

Li^+ (g) [-520 kJ/mol] > Na^+(g)[-406 kJ/mol]

88. Correct option is (c)



The structure of $\mathbf{O_2F_2}$ resembles that of H_2O_2, in its large dihedral angle, which approaches 90°. The reaction of fluorine with a dil. aqueous solution of NaOH gives OF_2 with sodium fluoride as a side-product.

$2F_2 + 2NaOH \rightarrow OF_2 + 2NaF + H_2O$

Oxidation (Reducing agent)

$$H_2S + 4\overset{(+1)}{O_2}F_2 \rightarrow SF_6 + 2HF + 4\overset{(0)}{O_2}$$

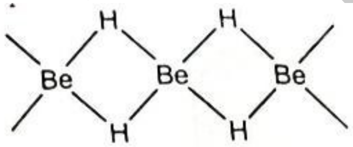
Reduction (Oxidizing agent)

89. Correct option is (a)

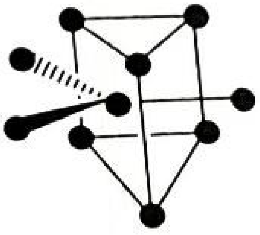
In fullerene the juncture bond (C=C) is the donor pi-bond. Hence, its common hapticity will be two

90. Correct option is (c)

- Alkali metal hydrides are saline hydride.
- BeH_2 has polymeric structure with 3c-2e bonding.



- Bigger metal hydrides are usually interstitial hydrides as H^- can be trapped in their bigger voids.
- $[TcH_9]^{-2}$ is trigonal tricapped prismatic.



91. Correct option is (a)

(A) The highest oxidation state +8 of group 8 elements is shown readily in oxides like OsO_4 and RuO_4 than in fluorides like RuF_8 and OsF_8 because these fluorides are unstable due to increased steric hinderance.

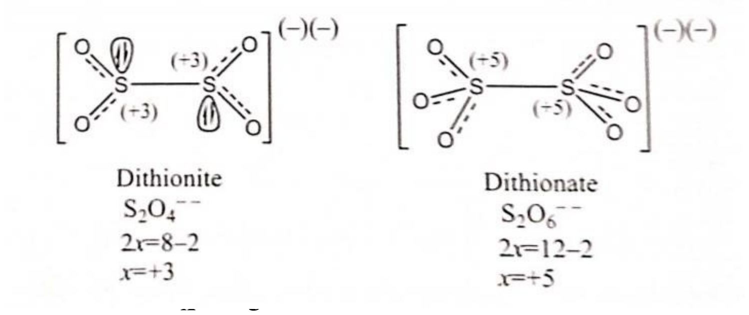
(B) Fe can exist in-2 formal oxidation state also in carboxylate like $[Fe(CO_4)]^{-2}$.

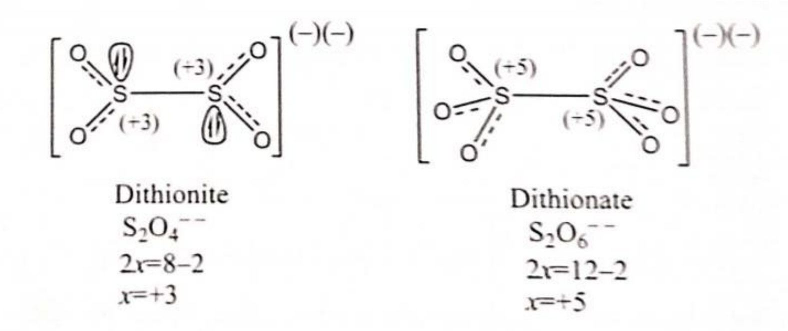
(C) Mn forms Mn(II) compounds easily but Tc and Re rarely form M(II) compounds as indicentis their standard reduction potentials.

Mn^{+2} (aq)+$2e^-$ → Mn(s). E^0 = -1.185 V
Negative value of E^0 indicates that the reaction Mn to Mn^{+2} is feasible
Tc^{+2} (aq) +2e → Tc(s). E^0 =+0.40V
Positive value of E^0 indicates that the reaction Tc to Tc^{+2} is not feasible.

92. Correct option is (a)

The structures of dithionite and dithionate are





93. Correct option is (b)

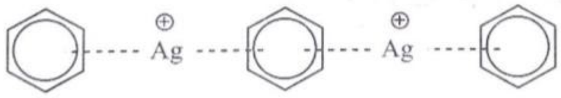
•On moving down in a group, the atomic radius generally increases. Even though d-orbital is present in Indium, its size is greater than that of aluminium as electron is added to 5s orbital which has much higher size than that of 3s orbital of aluminium. Even after contraction, size of 5s orbital is greater than that of 3s orbital. Due to higher atomic radius of In, its outer electrons experience lesser attraction towards nucleus hence, **($IE_1 + IE_2 + IE_3$)** for In is less than that of Al.

•On moving along the period, size decreases thus, effective nclear charge increases and hence I.E. increases. Therefore, IE_1 of Co is higher than that of Sc and IE_1 of Se is higher than that of Ga

• Nitrogen has stable half-filled $2s^2$ $2p^3$ configuration thus, has higher IE_1 than that of oxygen.

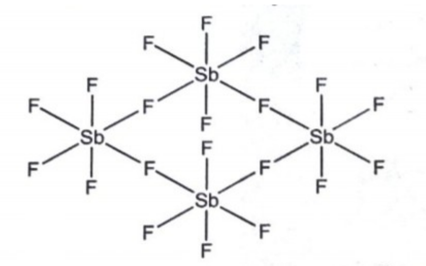
94. Correct option is (d)

Alkane is a hard base react with hard acid. Benzene acts as a soft base reacts with soft acid (Ag^+)



95. Correct option is (a)

a.$SbF_5 + 2HF \rightarrow [H_2F]^+ [SbF_6]^-$
b.In the solid state, SbF_5 is tetrameric thus, it has octahedral structure.



c.PF_3 acts as a strong π-acceptor ligand towards d-metals.
d.$AsCl_3$ may act as either a Cl^- donor or acceptor with an appropriate reagent. Thus, in presence of a chloride source, $AsCl_3$ can form complexes of type $[AsCl_4]^-$

96. Correct option is (b)

$2XeF_6 + SiO_2 \rightarrow 2XeOF_4 + SiF_4$
quartz (A)
$XeOF_4 + XeO_3 \rightarrow XeO_2F_2$
(A) (B)

97. Correct option is (a)

The table below defines energies and their proportional interactins

Type of interaction	Strength	Energy-distance function
Covalent bond	Very strong	Complex, but comparatively long range
Ionic bond	Very strong	1/r, comparatively long range
Ion-dipole	Strong	$1/r^2$, short range
Dipole-Dipole	Moderately strong	$1/r^3$, short range
Ion-induced dipole	Weak	$1/r^4$, very short range
Dipole-induced-dipole	Very weak	$1/r^6$, extremely short range
London dispersion force	Very weak	$1/r^6$, extremely short range

98. Correct option (c)

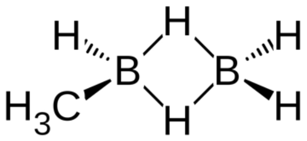
Generally for Nitrogen, oxygen and halogen family, electron gain enthalpy of 2nd period element is less than that of 3rd period element.

In group 16, O,S,Se and Te. If we apply general trend, that electron gain enthalpy decreases down the group, so the trend should follow O > S > Se > Te, but as mentioned elements of period 2 are generally have less electron gain enthalpy, because of their smaller and more compact size, which leads to repulsion between incoming and existing electrons. Thus oxygen has less electron gain enthalpy than others, so the order becomes S > Se > Te > O.

99. Correct option (b)

Statement (A) is correct as,

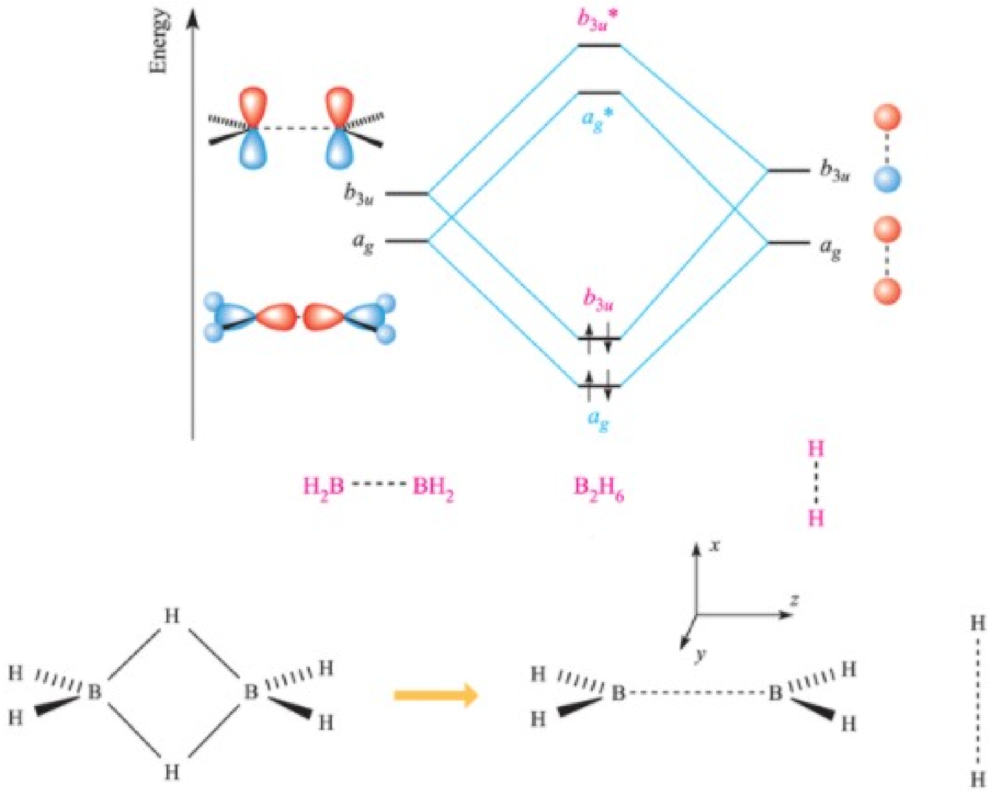
$$Et_V O \cdot BF_9 + NaBH_; \longrightarrow B_V H_b + Et_V O$$



Point group of B_2H_6 is D_{2h}, hence statement (B) is incorrect

Since, $B_2H_6 + 2NMe_3 \rightarrow 2BH_3 \cdot NMe_3$, thus statement (C) is correct

MOT of B_2H_6 is given by,



Hence, the molecule is Diamagnetic. Statement (D) is correct.

100. Correct option (d)

Reaction (i) and (ii) are possible but reaction (iii) cannot take place.

4

Nuclear Chemistry

Hints & Solutions

1. Correct option is (b)

With addition of α particle, atomic mass get increased by 4 and atomic number get increased by 2. With addition of β particle, atomic number get decreased by value of 1 and with release of β_{+}particle atomic number get decreased by 1.

Atomic mass of Y = 234+ 4 (due to addition of α) = 238

Atomic number of Y= 92-1 (due to addition of ^{2}-1) -2 (due to release of β_{+})

+2 (due to addition of α)

= 91

Thus, resulted nuclei is $_{91}\mathbf{Y}^{238}$

2. Correct option is (b)

In electron capture process a proton captures an electron from k-shell, and convert into a neutron. In this process an electron neutrino is also emitted. The reaction is as follows:

$$_{1}^{1}p \quad + \quad e^{-} \quad \rightarrow \quad _{0}^{1}n \quad + \quad \bar{\upsilon}_{e}$$

Proton **electron** **neutron** **neutrino**

Henuce, the products are neutron and neutrino

3. Correct option is (c)

In neutron activation analysis, the specimen is placed into a suitable irradiation facility and bombarded with neutrons. This creates artificial radioisotopes of the elements present. Following irradiation, the artifical radioisotopes decay with emission of particles or, more importantly gamma rays, which are characteristic of the elements from which they were emitted.

4. Correct option is (a)

The magic numbers of nucleons 2, 8, 20, 28, 50, 82, 126.

5. Correct option is (d)

The cross-section (σ) can be interpreted as the effective 'target area' that a nucleus interacts with an incident neutron. Larger the effective area, greater the probability for reaction

In reaction $\mathbf{{}_{92}U^{235} + {}_{0}n^{1} \rightarrow {}_{36}K^{94} + {}_{56}Ba^{140} + 2{}_{0}n^{1}}$ **,** one neutron react with $\mathbf{{}_{92}U^{235}}$ to give two neutron, which have more tendency to react with other radioactive nuclei. Thus, increases effective area for reaction.

6. Correct option is (c)

2, 8, 20, 28, 50, 82 and 126 are magic number.

7. Correct option is (a)

We have the relation between threshold energy and 'Q' of a reaction, as

$K_{Th} = -Q\left(\frac{\mathbf{M_a + M_A}}{\mathbf{M_A}}\right)$

Here, M_a = mass of moving projectile or bombarding particle

M_A = mass of stationary nucleus

Also, for endoergic reaction, Q > 0

Therefore, magnitude of threshold energy.

$K_{Th} = |-Q| \left(\frac{\mathbf{M_a + M_A}}{\mathbf{M_A}}\right); \left(\frac{\mathbf{M_a + M_A}}{\mathbf{M_A}}\right) > 1$

$|K_{Th}| > |Q|$

8. Correct option is (b)

In fission of U^{235} with thermal neutrons

(1) On the average, each fission of a U^{235} nucleus produces about 2.5 free neutrons

(2) Each fission produce 200 MeV energy

(3) Fission always occure in assymmetric fashion, it means number of nuclei undergoing unsymmetrical fission is maximum.

Hence, correct statement is (1) and (3).

9. Correct answer is (d)

10. Correct answer is (b)

The reaction which involve evolution of **γ** radiation are called radioactive capture reaction

$^{23}Na + {}^{:}_{-} n \rightarrow {}^{24}Na + \gamma$

11. Correct answer is (d)

The unstable nuclides like ^{233}U, ^{235}U and ^{239}Pu, undergo fission by thermal neutrons. ^{232}Th is a stable nuclei, compared to others.

12. Correct answer is (a)

The kinetic energy of deuteron (d-particle) is very low, hence it cannot excite ^{24}Mg nuclei.

13. Correct answer is (c)

Particles that are always to emit during positron emission

$^{1}P_{1} \rightarrow {}_{0}n^{1} + {}^{-}_{.} e + \bar{\upsilon}$ (antineutrino)

14. Correct answer is (a)

For an element the favourable characteristics both the target and the product in neutron activation is high neutron cross-section area of the target and long half-life of the product.

15. Correct answer is (a)

In carbon dating , $^{.0}{}_{/}C$ undergoes β- ray decay

$^{.0}{}_{/}C \rightarrow {}^{.0}{}_{1}N + \beta$

16. Correct answer is (b)

(A) ${}^{8}_{4}\mathbf{Be}$ $\mathbf{2}{}^{4}_{2}\mathbf{He}$ →

$\Delta m = 2x4.002603 - 8.005300 = -0.000094$

There is mass loss. Thus, energy evolve.

Therefore, exothermic

${}^{80}_{36}\mathbf{Kr}\rightarrow\mathbf{2}\ {}_{18}\mathbf{Ar}\quad{}^{\mathbf{40}}$

$\Delta m = 2\times 39.96238 - 79.81638 = 0.10838$

No mass loss, no energy realsed

Therefore, endothermic

17. Correct answer is (b)

${}^{.3}_{.-}\mathrm{Ne} \xrightarrow{-e^{6}_{45}\quad \text{positron)(}} {}^{.0}{}_{3}\mathrm{F}$;

${}^{.0}{}_{/}\mathrm{C} \xrightarrow{-e^{6}_{95}\quad \text{- particles}(\beta)} {}^{.0}{}_{1}\mathrm{N}$;

QUANTA POINT

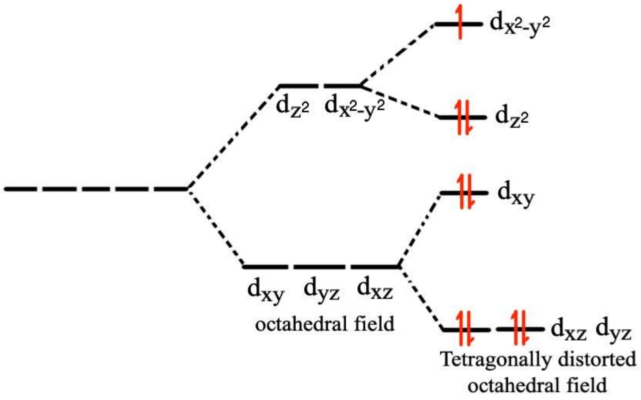
5

Inorganic Spectroscopy

Hints & Solutions

1. Correct answer: (b).

Gives the evidence that Cu on is present in tetragonally distorted octahedral field, the unpaired electron resides in the orbital d x^2-y^2



2. Correct answer: (c)

SnF_4 is ionic, here $Sn^{+4} = 5s^0$ so no quadrupole splitting.

SnCl4 is covalent, and Sn is sp3 hybridised, So there is s-electron density in the molecule.
Hence quadrupole splitting is possible.
R3SnCl is covalent, and Sn is sp3 so there is s-electron density in the molecule.
Hence quadrupole splitting is possible.

3. Correct answer: (b)

Both Fe(II) TPP and Fe(III)-TPP are square planar (because of tetradentate-planar, porphyrine type ligand), and both Fe(II) and Fe(III) are dsp2-hybridised, so there is s-electron density, which is responsible for their quadrupole moment and existence of mossbauer spectra.
So both Fe(II)-TPP and Fe(III)-TPP show increase in s-electron density, but Fe(II) has higher s-electron density. So Fe(II) has isomer higher shift (0.52 mms-1) than Fe(III) (0.45 mms-1).

4. Correct answer is (b).

At room temperature due to rapid interconversion of axial and equatorial F atoms, all the F will be equivalent. Hence ^{19}F NMR of PF_5 at room temperature will appear as doublet of ^5F.

5. Correct answer is (b)

Frequency shift (Δv) = $\frac{}{c}$ V v

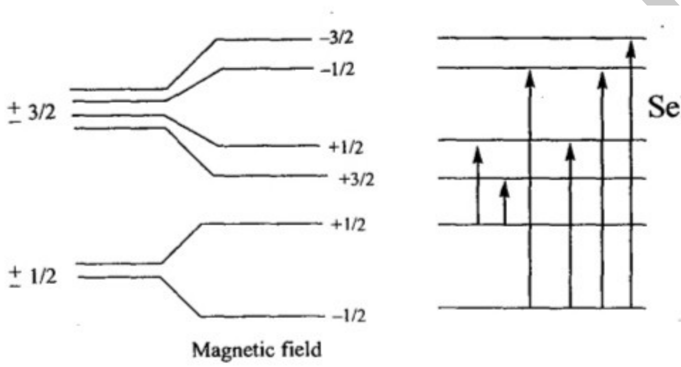
Where V =relative velocity of source and observer

v =frequency of emitted radiation

$$\Delta v = \frac{2.2\times\frac{10^{83}\ m}{s}\times 3.48\times10^{18}\quad Hz}{3\times10^{8}\quad m/s} = 2.55\times10^{7}\quad Hz = 25.5MHz$$

6. Correct answer is (d)

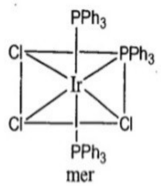
25.



Selection rule $\Delta M_I = 0.\pm1$.

Correct answer is (d).

7. Correct answer is (a)



Triple [illegible]cate 3 phosphorus atoms in the molecules in two sets

2P = d [illegible]

That is possible in mer-$[IrCl_3(PPh_3)_3]$

fac-$[IrCl_3(PPh_3)_3]$ will give singlet of 3P trans-[IrCI(Co)(PPh$_3$)$_2$] will give singlet of 2P.

[Ir(PPh$_3$)$_4$]$^+$ will give singlet of 4P.

8. Correct answer is (c)

The total numbers of fine and hyperfine EPR lines expected for octahedral high-spin Mn(II), I=5/2

Numbers of fine = No. of unpaired electron in Mn=5

Numbers of hyperfine EPR lines = No. of unpaired electron x (2nI+1)

n= no. of Mn atom = 1 , I= nuclear spin of Mn = 5/2

Numbers of hyperfine EPR lines $= 5 \times \left(2\times1\times \frac{E}{F} + 1\right) = 5\times6 = 30$

9. Correct answer is (b).

(1)Fe^3→High Spin-d^5 →Spherical electronic configuration

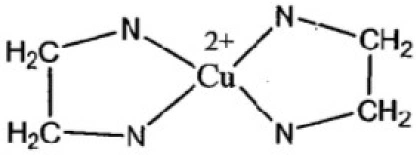
T^{E}_{FM} $\overset{F}{M}$ → No quadrupole splitting, singlet signal as shown in (B)

(2)Fe^2 →High-Spin- d^6→axial electronic configuration

T^{O}_{FM} $\overset{F}{M}$ →quadrupole splitting, gives doublet signal as shown in (A)

(iii) Fe^3 → Low-Spin- $\overset{E}{FM}$ $\overset{P}{M}$ → Axial electronic configuration quadrupole splitting,doublet signal as shown in (A)

10. Correct answer is (d)



n_N = number of equivalent nitrogen atoms

n_{Cu} = number of Cu atom

I_N = spin of one nitrogen

I_{Cu} = spin of copper

$$mI_{CH} = \pm\frac{1}{2},\ mI_N = 1;\ mI_{Cu} = \frac{3}{2}$$

$$\text{Multiplicity} = (2n_N I_N + 1)(2n_N I_{Cu} + 1) = (2\times4\times1+1)\left(2\times1\times\frac{3}{2}+1\right) = 9\times4 = 36$$

11. Correct answer is (d)

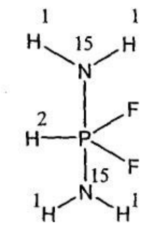
Recoil energy =R = $\frac{\mathrm{S}^{\mathrm{T}}}{\mathrm{FUV}^{\mathrm{T}}}$

$$= \frac{\mathrm{ERW}^{\mathrm{T}}}{\mathrm{FUV}^{\mathrm{T}}}\ \mathrm{X} \qquad eV$$

$$= 2.5\times10^{\mathrm{W}} = \frac{\mathrm{ERW}^{\mathrm{T}}\ \mathrm{X}}{\mathrm{QRZ\times ZRQ.E}}$$

E = $\sqrt{\frac{\mathrm{F.E\times QRZ\times ZRQ.E\times QP[}}{\mathrm{ERW}}} = 24.57\times10^{\mathrm{R}}$eV= 25 keV

12. Correct answer is (d)



^{1}H $I=\frac{1}{2}$; ^{15}N $I=\frac{1}{2}$; ^{19}F $I=\frac{1}{2}$

Four H^1 are equivalent. Two nitrogen are equivalent.

Two fluorine are equivalent. One ^{2}H is separate.

Multiplicity=$\left(2\times4\times\frac{\mathrm{Q}}{\mathrm{F}}+1\right)\left(2\times2\times\frac{\mathrm{Q}}{\mathrm{F}}+1\right)\left(2\times2\times\frac{\mathrm{Q}}{\mathrm{F}}+1\right)\left(2\times1\times\frac{\mathrm{Q}}{\mathrm{F}}+1\right) = 5\times3\times3\times2 = 90$

$4H^1$ $2N^{15}$ 2F 1H

13. Correct answer is (a)

If the system has an even number of unpaired electrons then zero field splitting within the ground state may result in the EPR transitions being undetectable and only one EPR signal is observe . Since Ni(II) octahedral complex has two unpaired electrons, therefore, number EPR signals is one.

14. Correct answer is (d)

^{129}I, ^{57}Fe , ^{121} Sb Mössbauer nuclei and they fulfuil all the properties for that **^{57}Co** is unstable nuclei which is used as y-source in the Mössbauer spectro photometer for ^{57}Fe study.

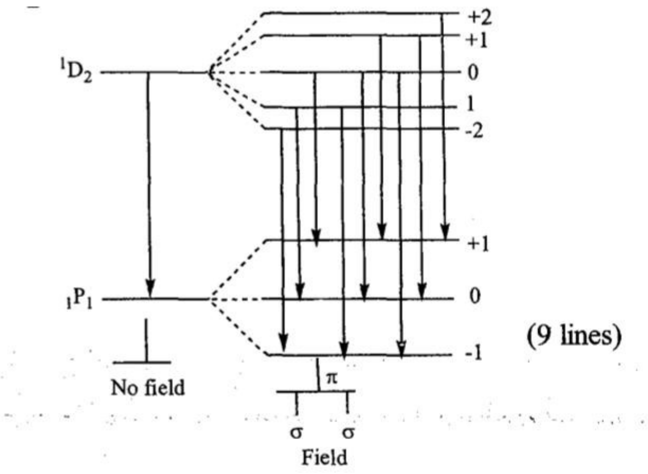
15. Correct answer is (b)

For systems with more than one unpaired electrons s >1/2 the ground state can be split in the absence of external magnetic field due to local site symmetry-the zero field splitting. For odd electrons systems, this results in pairs of energy levels known as Kramer's doublets. Since Cr(III) has three unpaired electrons, therefore number of Kramer's doublets in tetragonally distorted Cr(III) complex in zero field splitting is 2.

16. Correct answer is (a)

SELECTION RULE

$\Delta M_L = 0, \pm 1$ (for **Zeeman effect**)

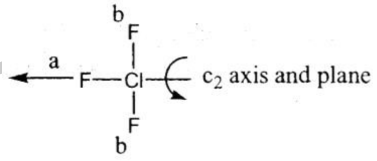


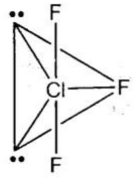
17. Correct answer is (c)

$$Doppler\quad shift = \frac{ijkkl\quad mn\quad imopVk\ \times npkqokr.Fs}{ijkkl\quad mn\quad tuMvw} = \frac{F.F\times QP^{xy}\ z/i\times R.O\{\times QP^{|\}}\ \sim\bullet}{R\times QP^{\}}\qquad z/i}$$

$=2.552x10^{€} = 25.5$ MHz

18. Correct answer is (a)





There are two types of F F_a , F_b

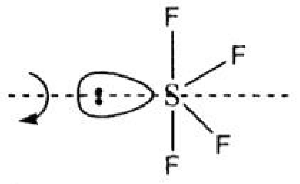
$^{19}F = F_b$ = doublet due to F_a

$^{19}F = F_a$ = triplet due to F_b

T shaped structure.

19. Correct answer is (d)

The low temperature , (-98°C) ^{19}F NMR spectrum of SF_4 - doublet of triplet



Equatorial F= 2x 2 x $\frac{Q}{F}$ + 1 = 3 , n=2 (axial F)

Axial F= 2x 2 x $\frac{Q}{F}$ + 1 = 3 , n=2 (Equatorial F)

One C_2 axis is present (passes through S and bisect the line joining the two F atoms each) $\boldsymbol{\sigma_h}$ is absent . $2\sigma_v$ present (molecular plane and the plane bisecting the line joining the two Fatoms passing through S).

Symmetry elements E , C_2 ,$2\sigma_v$

Point group symmetry = C_{2v}

20. Correct answer is (a)

Fe(II)= $3d^6$ $4s^0$, Fe(III)=$3d^5$ $4s^0$, Fe(IV)= $3d^4$ $4s^0$

Isomer shift in Mössbauer spectra depend on the s-electron density and d-electron density increase the s-electron density decrease the isomer shift increase the d-electron density increase the isomer shift.

So, so correct order, Fe (II) > Fe (III) >Fe (IV).

21. Correct answer is (d)

CD_3 (I_D= 1)

(2nI+1)= (2x3 x 1 + 1) = 7

22. Correct answer is (b)

Selection rule for EPR , $\Delta m_s = \pm1$, $\Delta m_l = 0$.

23. Correct answer is (d)

24. Correct option is (c)

Oxidation of Zn to Zn will be diamagnetic hence EPR inactive.

Fe and S - Inactive.

EPR spectroscopy generally used for the species have one or more unpaired electron.

Cu(II) are EPR active because non-paired electron.

25. Correct option is (c)

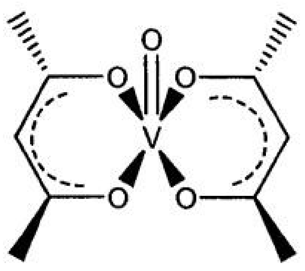
Mössbauer spectrum of a complex gives information about

(1) Oxidation state and spin state of metal

(2) Types of ligands co-ordinate to metal define by quardurpole splitting on the behalf of electronic environment of ligand symmetry.

(3) Also information about geometry of metal

26. Correct option is (a)



For vanadium, I= 7/2 . So, 2nI+1= 2(1)(7/2) + 1 = 8

So, in EPR spectrum it has two g values and it has two patterns of 8 lines each.

27. Correct option is (a)

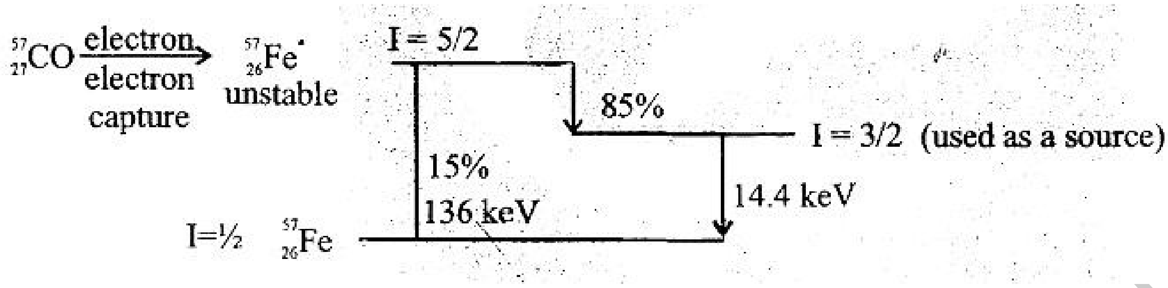
BH_3 part of the molecule **$Ph_3P.^{11}BH_3$**

^{1}H NMR spectrum $(2N_1I+1) \times (2N_2I+1) =$ (2x1x3/2+1)x (2x1x1/2+ 1) = 4x2=8

^{11}B spectrum $(2N_1I + 1) \times (2N_2I+1) =$ (2x3x1/2+ 1)×(2x1x1/2+ 1) = 4x2 = 8

28. Correct option is (c)

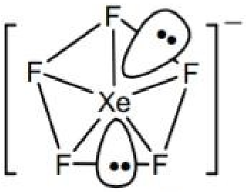
^{57}Fe* can be prepared by electron capture process from radioactive $^{57}_{F€}$CO.



29. Correct option is (c)

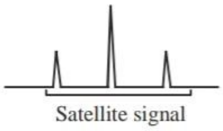
[XeF$_5$]$^-$ = $\frac{\{\bullet E \bullet Q}{E}$ = 7 = sp^{3}d^3 hybridzation

Shape = Pentagonal Planar



Pentagonal Planar

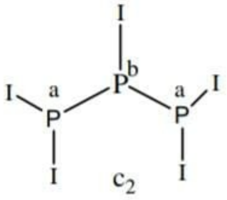
as 74% Xe are NMR inactive hence a singlet of five fluorine and due to 26% nuclei a doublet of satellite.



Hence, total number of signal is 3.

30. Correct option is (c)

Correct structure is



One C_2 axis and one plane of symmetry exist in this molecules,

So, two types of phoshphorous atoms

For ${}^{a}P$ (2NI+1)= [2x1x1/2+1] = 2 (doublet)

For ${}^{b}P$ (2NI+1) = (2x2x1/2+1) = 3 (triplet)

31. Correct option is (a)

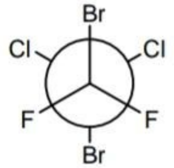
Number of hyperfine line (due to Cu and nitrogen)

$(2NI_{Cu}+1)\ (2NI_N+1)$

(2x1x3/2+1) (2×2×1+1)

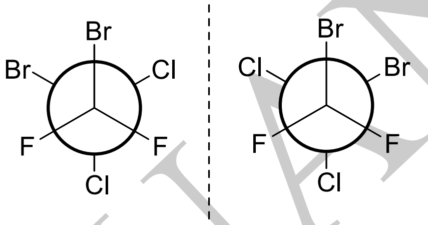
4x5=20.

32. Correct option is (d)



Both fluorine in same environment.

So, form doublet $(2NI_F+1)$=(2×1×1/2+1) =2

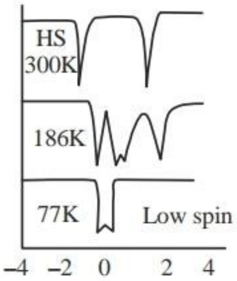


Both are mirror image to each other
but fluorine in different enviornment

(2x2x1/2+1) = 3 triplet

So, total number of line 2+3=5

33. Correct option is (a)



- Since NCS is ambidentate ligand therefore change in co-ordinate mode
- Change in the spin-state of iron at high temperature

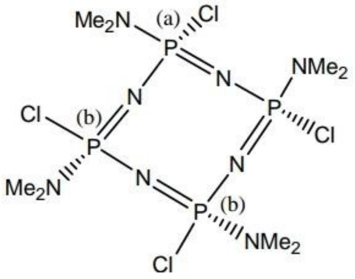
34. Correct option is (b)

$(R_3Ge)_2 \rightarrow 2R_3Ge$ (radical) in R_3Ge (radical)

Multiplicity = (2nI + 1) = 2x1x9/2+ 1 = 10 lines

^{73}Ge [I = 9/2]

35. Correct option is (a)



^{31}P {^1H} → (2NI+1)=[2×2×1/2+1]=3 (triplet)

^{31}P {^1H} → (2NI+1) = (2x2x1/2+1)=3 (triplet)

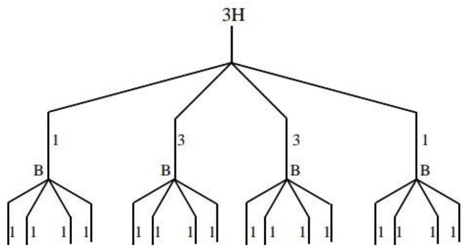
36. Correct option is (c)

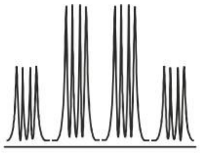
$H_3P.\ ^{11}BCl_3$

^{31}P NMR→($2NI_H$+1) for 3H=(2x3x1/2+1)=4(quartet)→1:3:3:1

P NMR → ($2NI_B$+1) for B = (2x3/2x1+1)=4(quartet)→1:1:1:1

Intensity ratio: 1:1:1:1:3:3:3:3:313:3:3:1:1:1:1



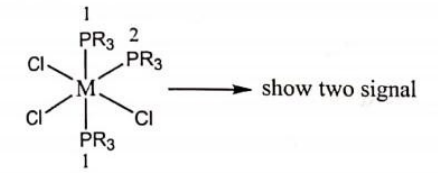


37. Correct option is (c)

In **CD_3** molecule => I = 1

Number of EPR lines= (2NI+1) = (2x3x1+1) =7

38. Correct option is (c)



mer-$[M(PR_3)_3Cl_3]$

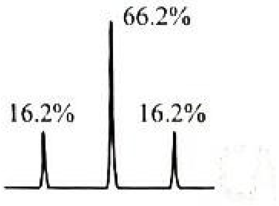
39. Correct option is (b)

Out of 100% molecule of cis-$[Pt(PEt_3)_2Cl_2]$, 33.8% $[Pt^{195}(PEt_3)_2Cl_2]$ having **doubled** satellite in ^{31}P NMR due to $^{1}J_{P\text{-}Pt}$ coupling and 66.2% $[Pt(PEt_3)_2Cl_2]$ having **Singlet** signals in ^{31}P NMR due to $^{1}J_{P\text{-}Pt}$ coupling absent.

Overall the ^{31}P NMR signal will be singlet signal with 33.8% doublet satellite as given below.

OR

The $^{31}P\ \{^1H\}$ NMR spectrum is comprised with satellite peak of a singlet signal.



40. Correct option is (b)

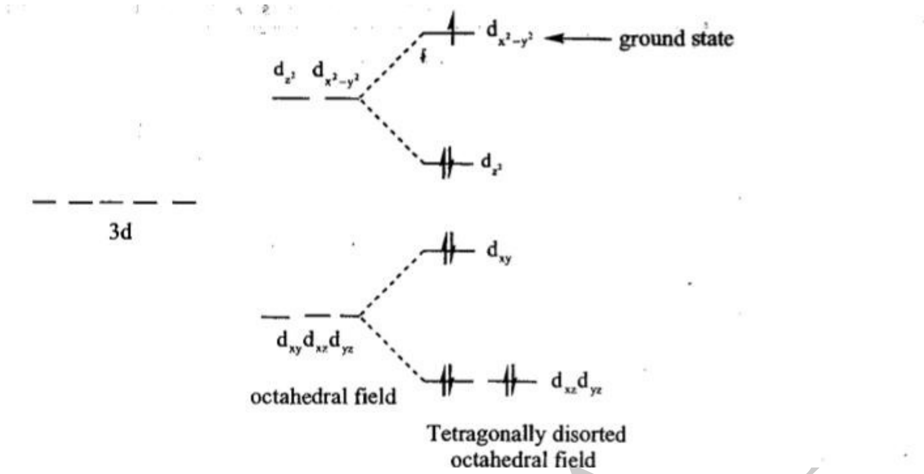
$[FeO_4]^{-2}$

- It is stable in strongly basic medium
- Powerful oxidizing agent
- The isomer shift of its Mossbauer spectrum is more negative compared to that of $FeCl_3$

41. Correct option is (a)

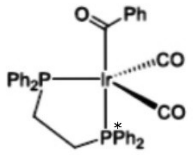
$g\parallel > \mathbf{g} \perp > \mathbf{g_2}$

the evidence that Cu on is present in tetragonally distorted octahedral field,



Ground state tetragonally elongation & unpaired electrons in $\mathbf{d}_{x^2-y^2}$

42. Correct option is (d)

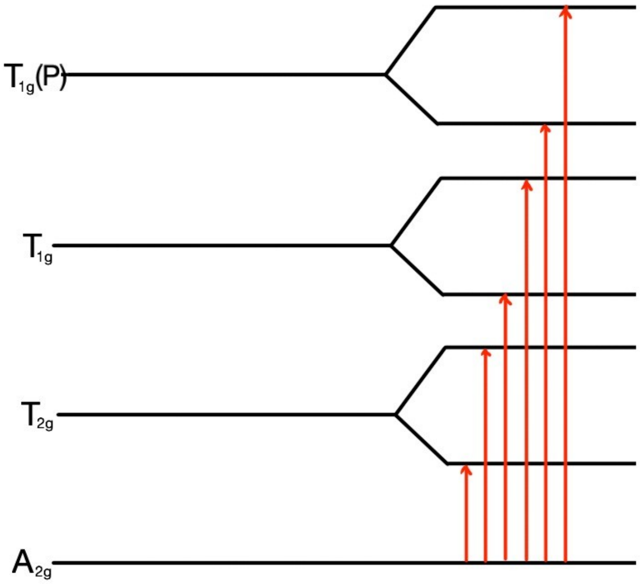


Both phosphorus are chemically different $^2J_{P-P}$ and $^3J_{P-P}$ and are possible,

Signal for =(2NI* +1)=[2x1×1/2+1]=2→ doublet

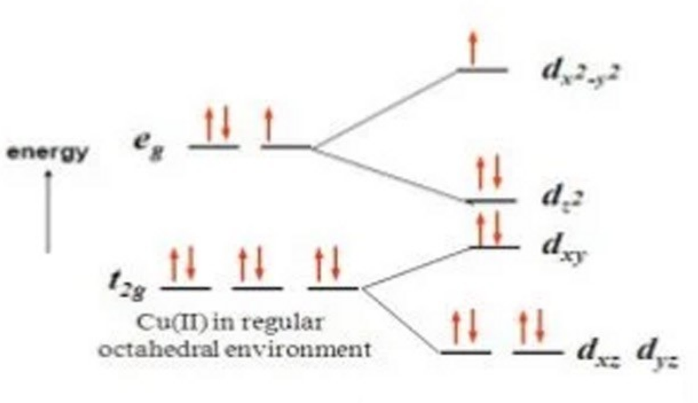
Signal for P* = (2NI +1)=(2x1x1/2+1)=2→doublet

43. Correct option is (c)



44. Correct option (a)

Selection rule for allowed transition is $\Delta M_f = \pm 1$ *and* $\Delta M_t = 0$, thus statement (A) is correct



In tetragonally elongated Cu(II) complex, more electron density is along d_z^2 orbital hence $g_{\parallel} > g_0$
Ground state for tetragonally compressed Cu(II) complexes is $d_{x2\text{-}y2}$.

QUANTA POINT

6

Lanthanides & Actinides

Hints & Solutions

1. Correct answer: (a)

(A) Correct, As 4f-electrons are too well shielded to interact, so they are like inert gas-type ion, like those of alkaline earth metals, that attracts ligands only by overall electrostatic forces.

(B) Correct, Lanthanides owing to the unavailability of orbitals for bonding, high basicity and rather large size of Ln3$^+$, form few complexes and mostly with oxygen or oxygen plus nitrogen chelating ligands such as -dietones, hydroxy acids EDTA etc. So, they rarely show isomerism and also lability of ligands make the isolation of isomers difficult.

(C) Incorrect, C.N. more than 8 are common, due to their larger size and smaller chelating ligand like,

NO_3^- SO_2^-4etc.eg. $[Ce(NO_3)6]_2^-$,C.N=12

(D) Correct, As 4f electrons are well shilded from external fields by the overlying 5s and 5p elec trons.Thus the magnetic effect of orbital motion is cannot be neglected.

2. Correct answer: (a)

As we move from 2d row transition element (Zr) to 3 row transition element (Hf), size should increase, but due to lanthanide contraction offset the increase, so Zr and Hf have almost similar size.

3. Correct answer : (d)

$_{64}$Gd = [Xe]4f^7 5d^{1}6s^2, Gd^{+2}=[Xe]4f^7 5d^1 6s°

Removal of electrons takes place from the outermost orbital only.

4. Correct answer : (a)

Uranium fluorides co-precipitate with CaF_2

5. Correct answer is (d)

Sm^{3+}due to spin-orbital coupling

6. Correct answer is (a)

$Al(OH)_3$ Amphoteric whereas hydroxides of lanthanoids are all base.

7. Correct option (b)

$Eu^{+2} \rightarrow 4f^7 \rightarrow$ Half-filled → stable

$Yb^{2+} \rightarrow 4f^{14} \rightarrow$ Completely filled → stable

8. Correct answer is (d).

Smaller the size of Lu^{3+} ion, higher will be the partition coefficient**.**

9. Correct answer is (d)

Since size of Lu is smallest, therefore $Lu(OH)_3$ complex most easily formed with NaOH and dissolves.

$Lu(OH)_3 + 3OH^- \rightarrow [Lu(OH)_6]^{3-}$

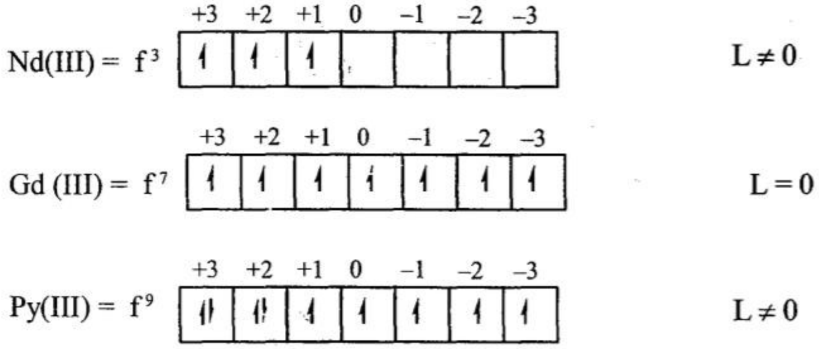
10. Correct answer is (a)

The electronic configuration of Gd^{+3} and Lu^{+3} are $4f^7$ and $4f^{14}$, for this ions total angular momentum is zero i.e. there is no orbital contribution. Therefore, calculated and observed values of magnetic moment are closest for this pair.

11. Correct answer is (a)

$\mu_{observed} = \mu_s + \mu_l$

$\mu_{observed} = \mu_s$ only if $\mu_l = 0$



$L = \Sigma m_\ell$ So, μ_ℓ will be zero only for Gd (III) f^7.

12. Correct answer is (b)

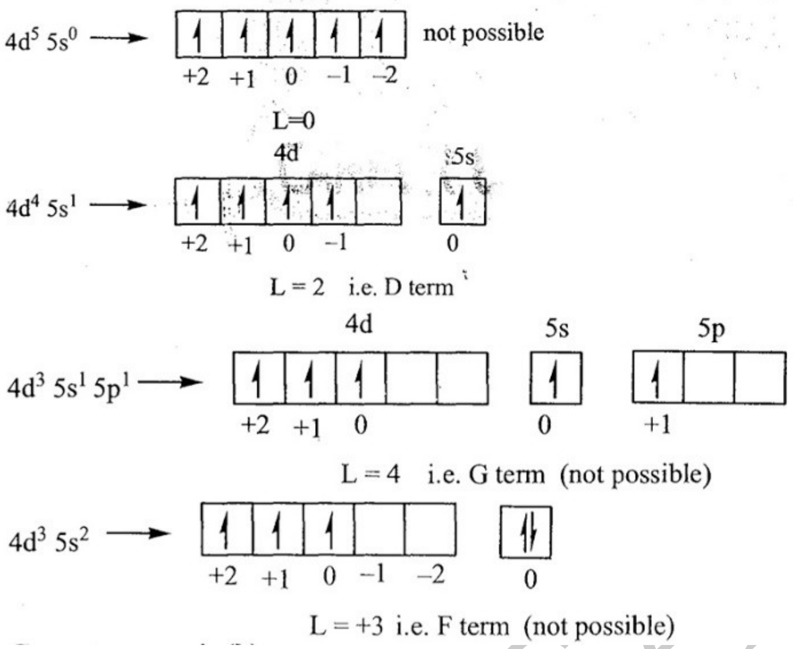
NTA POINT

Ground state term → ^6D

2s+1=6

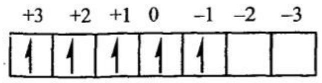
2s=5 => s =5/2 i.e. five unpaired electrons

For D, term L=2



13. Correct answer is (b)

Sm→ [Xe]$4f^6\ 5d^0\ 6s^2$, Sm^{+3} → [Xe]$4f^5\ 5d^0\ 6s^0$



$S=\frac{5}{2} \quad \Rightarrow 2s+1=2\times\frac{5}{2}+1=6$

L = +3 + 2 + 1 − 1 = 5

0 1 2 3 4 5

S P D F G H

J=|L+S|…|L-S|

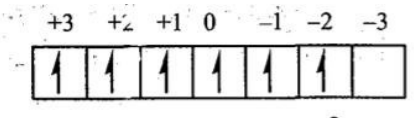
=|5+5/2|…. |5-5/2|

= 15/2 5/2

$^6H_{15/2}$, $^6H_{5/2}$

Ground state term= $^6H_{5/2}$

Eu = [Xe]$4f^7\ 5d^0\ 6s^2$, Eu= [Xe] $4f^6\ 5d^6\ 6s^0$



$S=\frac{6}{2} \Rightarrow 2S+1=2\times\frac{6}{2}+1=7$

L=3+2+1+0-1-2-3

0 1 2 3

S P D F

J=|L+ S|……|L-S|

=|3+3|….. |3-3|

=6 0

$^7F_6$ $^7F_0$

Ground state term $^7F_0$

14. Correct answer is (b)

Sm $4f^6$ $5s^0$ $6s^2$

Eu $4f^7$ $5s^0$ $6s^2$

Sm can accept one electron and become half field. So, it is better oxidant.

15. Correct answer is (a)

The retention of ion in exchanges column depends upon the size of ion. Smaller the size of cation, stronger will be its binding ability. In cation exchanger column the aqueous solution of ion is passed where binding ability depends upon hydrated radii.

K^+ (aq) < Na^+ (aq) < Li^+ (aq)

Since, size of hydrated ion increases as shown above.

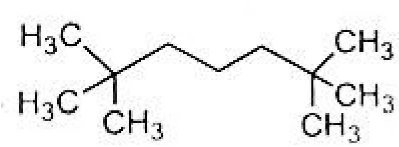
Therefore, binding ability decreases as K^+ (aq) > Na^+ (aq) >Li^+ (aq)

Ag^+(aq) show polarization effect, hence, has high binding ability.

Correct order : **$Ag^+ > K^+ > Na^+ > Li^+$**

16. Correct answer is (b)

Dipivaloylmethane, form chelats with lanthanides



17. Correct option is (a)

$2UO_2^{+}$ (aq) + $4H^{+}$ (aq) → U^{+4} +UO_2^{+2} (aq) + $2H_2O$

UO_2^{+} disproportionates more easily than UO_2^{+2} [correct]

(B)U_3O_8 is most stable oxide of U. U_3O_8 is stable at high temperature [correct]

(C)$[UO_2(NO_3)_2(H_2O)_2]$ co-ordination number = 8 [incorrect]

(D)UO_2^{+2} is linear $[O{=}U{=}O]^{+2}$ [correct]

18. Correct option is (d)

$(NH_4)_2[Ce(NO_3)_6]$(Z)

(1) NO^{-}_3 behaves as bidentate ligand. Hence, C.N = 12

(2) Ce^{+4} has no unpaired electron hence dimagnetic not paramagnetic.

(3) Ce^{+4} has higher oxidation state hence behave as oxidising agent.

(4) $(NH_4)_2[Ce(NO_3)_6]$ on reaction with Ph_3PO gives $[Ce(NO_3)_4(Ph_3PO)_2]$ having . C.N.=10. Hence correct statement.

$OPPh_3$ = mono dentate ligand; NO_3= bidentate

19. Correct option is (a)

The Eu and Yb donate two electrons in their metallic bonding unlike other lanthanoids which donate three electrons.

This is due to Eu^{+2} ($4f^7$) and Yb^{+2} ($4f^{14}$) stable configurations

$Ln \rightarrow Ln^{+3} + 3e^{-}$

$Eu \rightarrow Eu^{+2} + 2e^{-}$ ($4f^7$) half filled stable kernel

$Yb \rightarrow Yb^{+2} + 2e^{-}$ ($4f^{14}$) full filled stable kernel

Hence, they show abnormally larger sizes than other lanthanoids.

Eu =1.99Å , Yb=1.94 Å

20. Correct option is (a)

(a) There is no good agreement between the calculated ($\mu_g = \sqrt{J(J + g\,1)}$ B.M.) and experimental magnetic moments for Eu^{+3} and Sm^{+3} ions because of low value of spin orbit coupling constant. Therefore, the ground state and the first excited states become equally populated, due to the thermal motion become equally populated due to thermal motion. Hence, the observed magnetic moment of Eu^{+3} at room temperature is higher than that calculated from spin-orbit coupling.

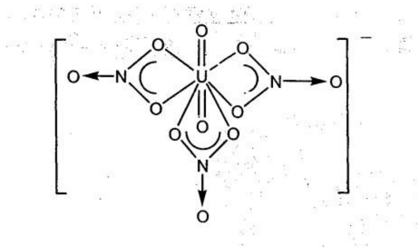
(b) Lanthanide oxides are predominantly basic in nature.

(c) The Sm(II) ion has 4f configuration. Thus, in Sm (II) 4f subshell is not half filled

(d) Since the chemical properties of the tripositive lanthanide ions (due to their similar size) they cannot be separated easily by chemical method. Instead they can be separated by ion exchange chromatography.

21. Correct option is (a)

$[UO_2(NO_3)_3]^{-1}$



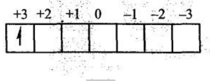
Co-ordinate number is 8 and geometry is hexagonal bipyramidal.

22. Correct option is (d)

Lande's splitting factor g is calculated as

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{(J(J+1)}$$

$Ce^{+3} = f^1$



L=3

S=½

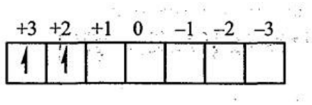
J=|L-S| for orbital less then half filled

J=|3-½|=5/2

$$g= 1+\frac{5/2\ (5/2+1)\ +1/2(1/2+1)-\ 3(3+1)}{(\times 5/2(5/2+1)}$$

g= 6/7

$Pr^{+3} = f^{3}$



L=3+2 =5

S= 1

J=|5-1|=4

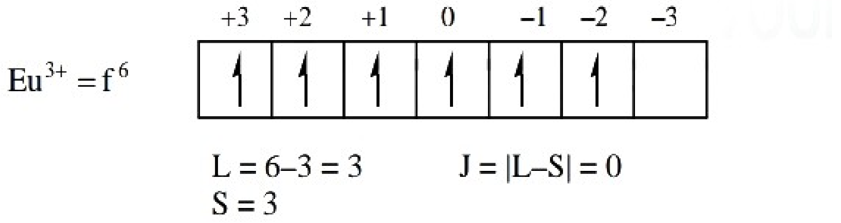
$$g= 1+\frac{4\ (4+1)\ +1(1+1)-\ 5(5+1)}{(\times 4(4+1)} = \frac{0}{1}$$

23. Correct option is (c)

A magic number is a number of nucleons (either protons or neutrons separately) such that they are arranged into complete shells , within atomic nucleus ,the seven most widely recoginized magic numbers 2, 8, 20, 28, 50, 82 and 126 are magic number.

24. Correct option is (c)

The calculated and observed magnetic moments of Eu^{+3} aqua complex are 0 and ~3.5 . The reason is that with the spin orbital coupling constant is only about 230 cm . This means that the difference in energy between the ground state and next excited state is small .So most of electrons goes to excited state and paired .



Hence $\mu = \sqrt{J(J+1)} = 0$

25. Correct option is (a)

(a) Lu(III) = [Xe] $4f^{14}\ 5d^{0}\ 6s^{0}$ hence diamagnetic

(b) EuI_2 has metallic lustre

(c) Ce(IV) used as oxidising agent

(d) Tb(III) – f^8 has pink colour

26. Correct option is (a)

(A) Due to more expansion of 5f orbital actinoids has more tendency to release electron hence have more tendency to show oxidation state greater than +3 compared to Lanthanoids

(B) Actinoids (III) show either f-d or f-f transition, but no d-d transition

(C) UO_2^{+2} and PuO_2^{+2} are stable

(D) All the actinoids have radioactive isotopes

27. Correct option is (b)

Gd^{+3} ion show isotropic magnetic susceptibility

28. Correct option is (a)

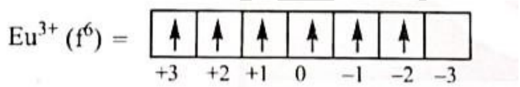
Pink → Sm(III)

Red → Eu(III)

Green → Tb(III)

Blue → Tm(III)

29. Correct option is (b)



L=3 = F

S=3 2S+1=7

J= |L-S| =|3-3|=0

Hence, $^7F_0$

Since, J=0 hence μ should be zero but due to population of higher J level μ >0. But as temperature decreases population in excited J level decreases hence magnetic moment approaches to calculated value i.e. zero.

30. Correct option is (c)

In hexahydrate of gadolinium (III) chloride, six H_2 O molecules and $2Cl^-$ ions coordinate to the metal cation resulting in a coordination number of 8.

$GdCl_3.6H_2O = [GdCl_2(H_2O)_6]^+ Cl^-$

31. Correct option is (d)

The configurations and magnetic moment are

M^{+3}	f^n	$\mu_{observed}$	$\mu_{calculated}$
Gd^{+3}	$4f^7$	7.97	7.94
Lu^{+3}	$4f^{14}$	0	0
Tb^{+3}	$4f^8$	9.8	9.7
Sm^{+3}	$4f^5$	1.64	0.85
Eu^{+3}	$4f^6$	3.36	0

- Gd^{+3} (f^7) and Lu^{+3} (f^{14}) follow spin only formula $\sqrt[5]{n(n+2)}$ μ =
- While for remaining $\mu(eff) = g\sqrt[5]{J(J+1)}$ is valid

32. Correct option is (a)

Ac shows only +3 oxidation state because it achieve nearest noble gas configuration of Rn.

Lr shows only +3 oxidation state because it achieve fully filled [Rn] $5f^{14}$ configuration.

33. Correct option is (c)

a.Lu^{+3} = Completely filled f^{14} configuration thus, no f-f transition.

b. For Tb^{+3}, the main emissions responsible are $^5D_4 \rightarrow {}^7F_n$ (n = 6 - 0) with $^5D_4 \rightarrow {}^7F_5$ the strongest, whilst for Eu^{+3} , $^5D_0 \rightarrow {}^7F_n$ are seen (n= 4-0) with the transitions to $^7F_0$, $^7F_1$ and $^7F_2$ the most useful

c. Overlapping J levels are observed for Sm^{+3}

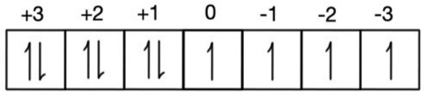
34. Correct option (a)

The value of $\mu_{9::}$ can be calculated using formula; $\mu_{9::} = g_J\sqrt{J(J+1)}$

Where,

$$g = 1 + \frac{S(S+1) - L(L+1) + J(J+1)}{2J(J+1)}$$

for f^{10} configuration



Here, S = 2, L = 6 and J = 8,

Solving for g will give, g = 1.25

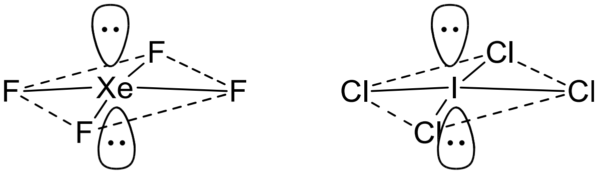
Hence $\mu_{9::} = 10.6$

Chemical Bonding

Hints & Solutions

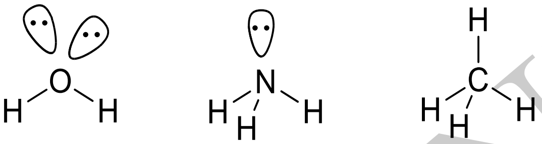
1. Correct answer: (b)

Explanation: Both XeF_4 , ICl_4^- have 2 lone pair of electron. The shape being square plannar with hybridization sp^3d^2



2. Correct answer: (c)

Explanation:

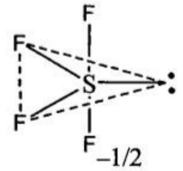


All three molecules have same hybridization sp^3

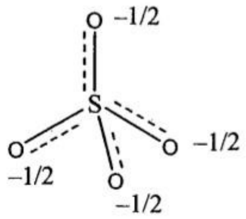
Bond angles and bond distances are different, shapes are bent, pyramidal and tetrahedral respectively.

3. Correct answer: (b)

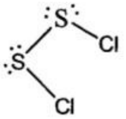
Explanation: SO_4^{-2} is tetrahedral.



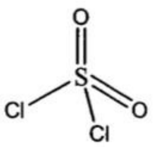
(SF$_4$)
Sea-Saw



(SO$_4^{2-}$)
Tetrahedral



(S$_2$Cl$_2$)
bent shape around
both s-atom



distorted tetrahedral
(Because all bonds are
not equivalent, so repulsion
will be different between
different bonds.)

4. Correct answer: (a)

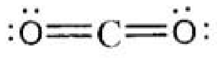
Explanation **:** Taking x-axis as internuclear axis.

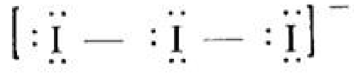
$N_2 = \sigma^2_{1s}\ \sigma^2_{1s^*}\ \sigma^2_{2s}\ \sigma^2_{2s}{}^*\ \pi^2_{2py}\ \pi^2_{2pz}\ \sigma^2_{2px}$

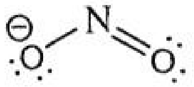
$O_2^+ = \sigma^2_{1s}\ \sigma^2_{1s^*}\ \sigma^2_{2s}\ \sigma^2_{2s}{}^*\ \pi^2_{2px}\ \pi^2_{2py}\ \sigma^2_{2px}\ \pi^1{}^*_{2pz}\ \pi^1{}^*_{2py}$

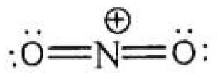
5. Correct answer: (b)

Explanation: I^-_3 is linear with highest number of lone-pairs (9 lone-pairs)

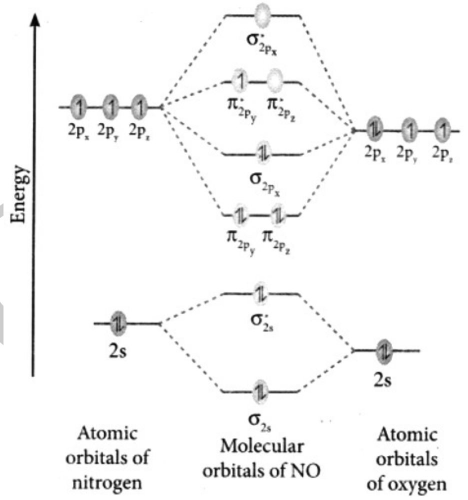


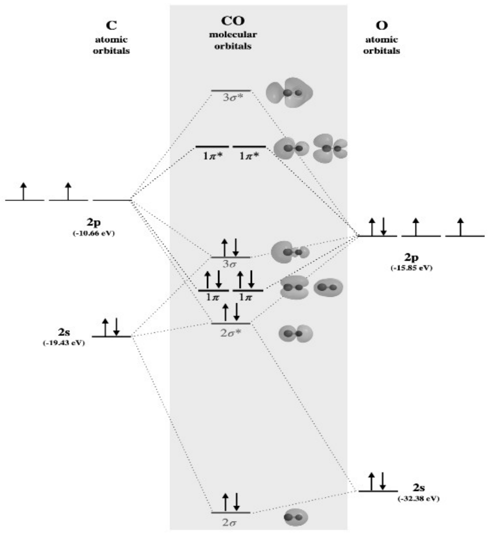






6. Correct answer is (a)





Number of electrons in antibonding MO of NO = 1
No electron is present in antibonding MO OF CO=0
So, number of antibonding MO is zero .

7. Correct answer is (b)

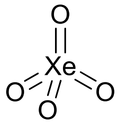
(A) **N_3^-** → linear, **XeF_2**, → Linear

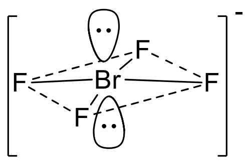
(B) [**ClF_2**]$^+$ → Bent, **[ICl_2]$^-$** → Linear

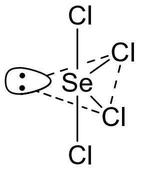
(C) **[ICl_4]$^-$,** → square planar, **[$PtCl_4$]$^{2-}$** → square planar

(D) **XeO_3**→ Trigonal pyramidal, **SO_3**→ Trigonal planar

8. Correct option is (c)

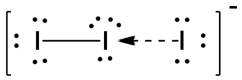




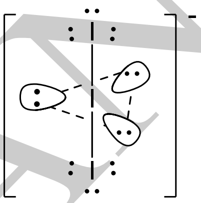


9. Correct answer is (d).
Size of d-orbitals decrease with decrease in size of element. The decreasing order of size is
Si > P > S > Cl.
Therefore decreasing order of size of d-orbitals is Si> P > S >Cl.

10. Correct answer is (d).
Number of lone pair of electrons = 9

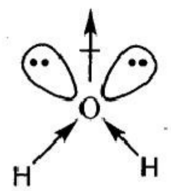


or

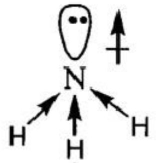


11. Correct answer is (d).
Smaller the internuclear distance between two atoms, stronger will be the π bonds. The increasing or due of inter nuclear distance is Cl-O < S-O <P-O <Si-O Therefore strength of pπ –dπ bonding is Cl-O> S-O>P-O>Si-O

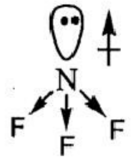
12. Correct answer is (d)



More electronegativity difference between O and H



Less electronegativity difference between N and H



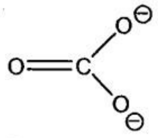
E.N. of F is greater than that of N

Therefore, order of dipole moment is $\mathbf{H_2O > NF_3 > NH_3}$

13. Correct answer is (d)

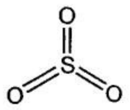
$\mathbf{CO_3^{-2}}$ **:** sp²-hybridization (Trigonal planar)
$\mathbf{SO_3}$ **:** sp²-hybridization (Trigonal planar)
$\mathbf{XeO_3}$ **:**sp-hybridization. (Trigonal pyramidal)
$\mathbf{NO_3}$ **:**sp²-hybridization (Trigonal planar)

$\mathbf{CO_3^{2-}}$



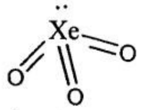
sp^2-hybridization (Trigonal planar)

$\mathbf{SO_3}$



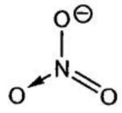
sp^2-hybridization (Trigonal planar)

$\mathbf{XeO_3}$



sp^3-hybridization (Trigonal pyramidal)

$\mathbf{NO_3^-}$



sp^2-hybridization (Trigonal planar)

$\mathbf{CO_3^{-2}}$,$\mathbf{SO_3}$, and $\mathbf{NO_3^{-2}}$, have planar structure.

14. Correct answer is (c)

40. When a hydrogen atom is placed in an electric field along the y-axis. The magnetic moment i.e electron density will he oriented along y-axis and therefore the orbital that mixes most with the ground state 1s orbital is $2p_y$.

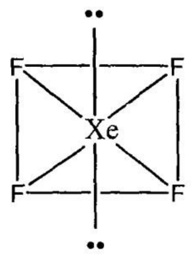
15. Correct answer is (d)

Among given compounds NF3 is not hydrolyse easily because, the more electro negative F atom strongly attracts the electrons present in N atom and they are no longer available to get hydrolysed. $BiCl_3$ is not readily hydrolysed by water to give BiOCl.

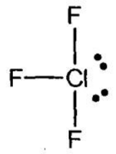
$$BiCl_3 + H_2O \rightarrow BiOCl + 2HCl$$

But BiOCl redissolve in conc. HCI to produce BiCl, after evaporation. It has quasi molecular structure. PCl_3 is easily hydrolysed by water.

16. Correct answer is (a)



Number of lone pair = 2



Number of lone pair =2

17. Correct answer is (c)

More than 8 electrons in the valence shell of P in $\mathbf{[PF_6]^-}$

18. Correct answer is (b)

$\mathbf{B_2 = \sigma^2_{1s}\ \sigma^2_{1s*}\ \sigma^2_{2s}\ \sigma^2_{2s}*\ \ \pi^1_{2px}\ \pi^1_{2py}}$

B.O. = $\frac{456}{7} = 1$

If an electron is added to B_2, then will go bonding to π -orbital.

B.O. becomes= = $\frac{;56}{7} = 1.5$.

19. Correct answer is (b)

Li = $1s^2\ 2s^1\ 2p^0$

Li^{+2} $1s^1\ 2s^0\ 2p^0$ (hydrogen like)

$Be^{+2} = 1s^2\ 2s^0\ 2p^0$

$H^- = 1s^2\ 2s^0\ 2p^0$

Li has one electron in 2s and no electron in 2p hence the energies of 2s and 2p orbitals will be different.

Li^{+2} has only one electron in $1s^1$ hence will have no screening effect

Therefore, 2s and 2p will have same energies.

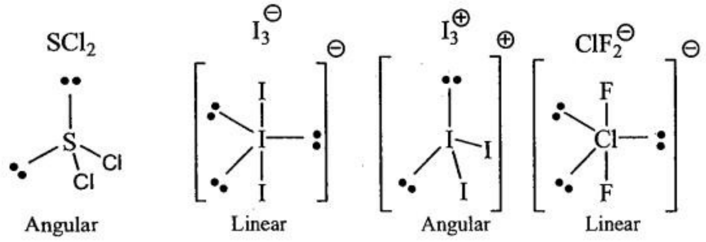
20. Correct answer is (c)

If a homonuclear diatomic molecule is oriented the z-axis, then linear combination of p_Z orbitals of two atoms form σ-orbitals.

The molecular orbitals formed by linear combination of p_X or p_Y orbitals of two atoms is π.

21. Correct answer is (c)

Number of valence electrons in $\mathbf{I_3^+}$ central atom are 8 while in $\mathbf{I_3^-}$ are 10 and hence the geometries are tetrahedral and trigonal bipyramidal.



22. Correct answer is (b)

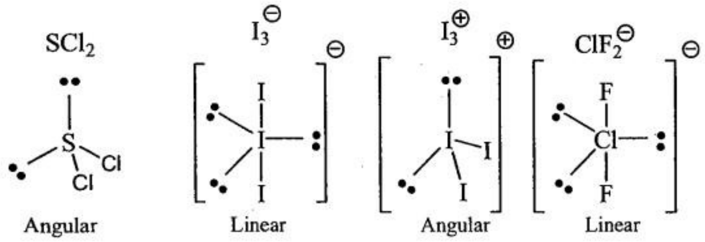
(I) SCl_2 b.p.=2 l. p. =2 Stearic number (S)=4

(II) I_3^- b.p. = 2 l. p. =3 (S)=5

(III) I_3^+ b.p. = 2 l. p. =2 (S)=4

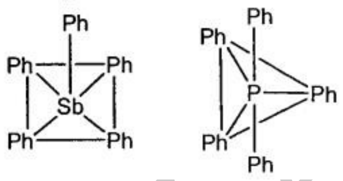
(IV) ClF_2^- b.p. = 2 l. p. =2 (S)=4

Shapes of species are



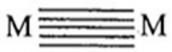
23. Correct answer is (b)

$SbPh_5$ is square pyramidal while PPh_5 is trigonal bipyramidal.
This is due to size of central atom. 'Sb' is bigger than 'P', therefore favour square planar while small sized 'P' favour trigonal bipyramidal



24. Correct answer is (c)

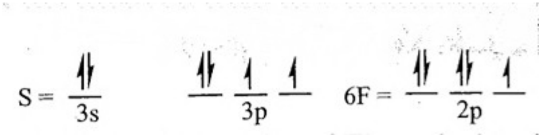
A maximum five 'd' orbitals can form bonding with each other



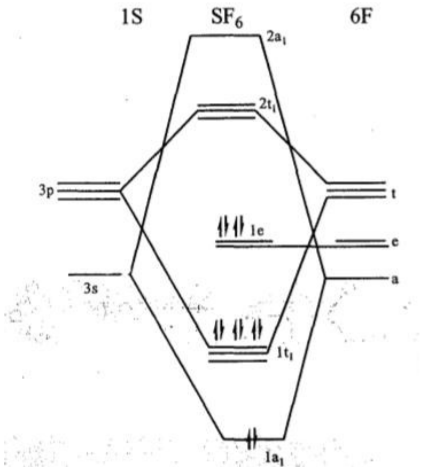
σ bonds ⟹ 1
π bonds ⟹ 2
δ bonds ⟹ 2

25. Correct answer is (a)

In the formation of SF_6 the following atomic orbitals are involved.



The 3s, 3p of 's' and $2p_z$ of 'F' are mixed to give ten MO's. Calculations indicate that four of orbitals will be bonding and four of orbitals will be bonding and four will be antibonding. The remaining two will be non-bonding. There are 12 electrons to be filled in ten MO's. The first two can enter $1a_1$ and the next six can in it. The remaining four fill the non-bonding pair of orbitals. Thus it gives $1a^2$ $1t^6$ e^4 gives as configuration. This gives the molecular diagram of SF_6, as

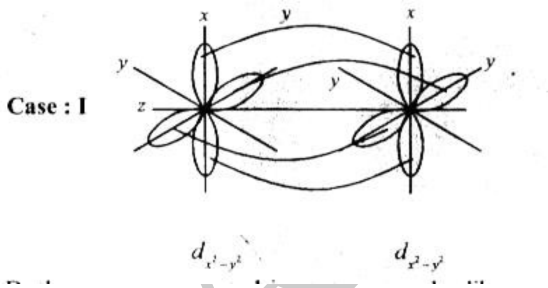


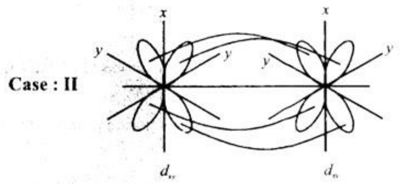
26. Correct answer is (a) & (c)

A **δ** -bond involves the overlapping of eight lobes by facewise overlapping. This can take place by ‘d’-orbitals and ‘f’ orbitals. In 'd' orbitals following two possibilities are

Case-I: $d_{x^2-y^2} + d_{x^2-y^2} \rightarrow \boldsymbol{\delta}$ bond

Case-II: $d_{xy} + d_{xy} \rightarrow \boldsymbol{\delta}$ bond.

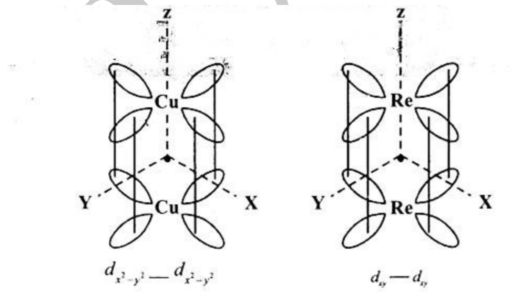




Both cases are reported in many examples like.

Case-I is reported in dimeric copper acetate (II)

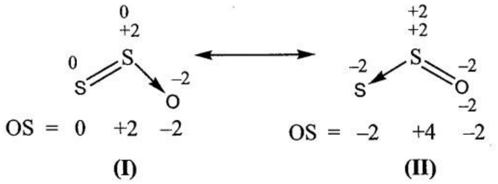
Case-II is reported in $Re_2Cl_8^-$



Hence, options (a) and (c) are correct

27. Correct option is (a)

The structure of S_2O show resonance as



Hence, the probable O.S. of 'S' are (0 and +2) from structure 'T' and (-2 and +4) from structure II.

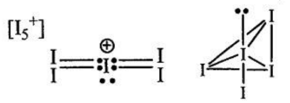
28. Correct option is (b)

$[Br_3]^+$ = Br. Br_2^+

$S = \frac{;>75?}{7} = 4 = sp^3$

Therefore, geometry = tetrahedral.

$[I_5]^+$

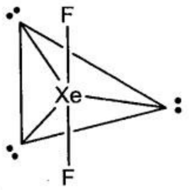


geometry = trigonal bipyramidal, sp^3d hybridisation)

29. Correct option is (c)

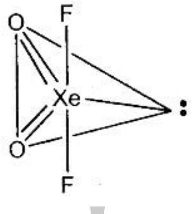
XeF_2 ; S = steric number = $\frac{@AB}{B}$ =5

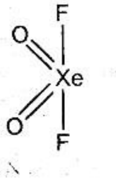
Therefore, G = Geometry = trigonal bipyramidal (TBP)



Hence, the shape linear Xe

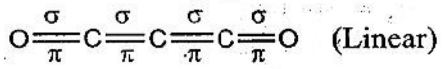
XeO_2F_2 s= $\frac{@AB}{B}$ =5 Geometry =TBP





30. Correct option is (a)

The structure of C_3O_2 (carbon suboxide) is



4σ and 4π

31. Correct option is (b)

In IF_7 and $Fe(CO)_5$, the rearrangement is so fast that axial and equatorial ligands cannot be differentiate by spectroscopy). The molecules in which rearrangement leads to configuration which are chemically equivalent are called fluxional molecule.

32. Correct option is (c)

The Mo configuration of $\mathbf{N_2}$and $\mathbf{N_2^+}$ are

$\mathbf{N_2} = \sigma_{2s}^2\ \sigma_{2s*}^2\ \pi_{2px}^2\ \pi_{2py}^2 \sigma_{2pz}^2$

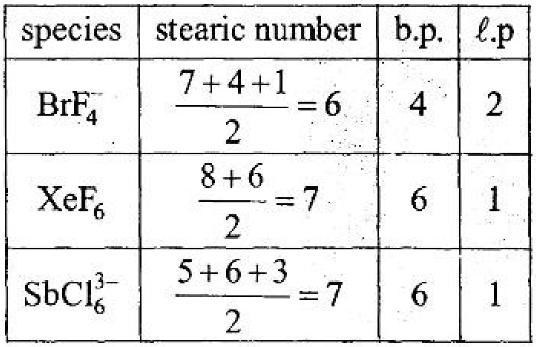
B.O.= $\frac{852}{2}$ **=3**

$\mathbf{N_2^+} = \sigma_{2s}^2\ \sigma_{2s*}^2\ \pi_{2px}^2\ \pi_{2py}^2 \sigma_{2pz}^1$

B.O.= $\frac{752}{2}$ =2.5

$N_2 \rightarrow N_2$ (Bond order decreases)

33. correct option is (c)



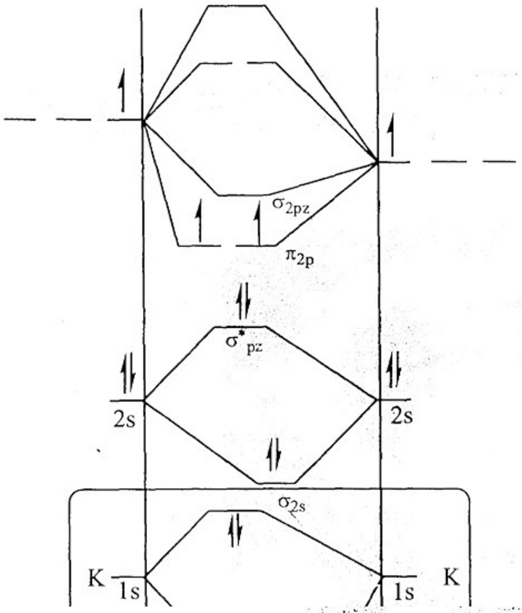
species	stearic number	b.p.	ℓ.p
BrF_4^-	$\frac{7+4+1}{2}=6$	4	2
XeF_6	$\frac{8+6}{2}=7$	6	1
$SbCl_6^{3-}$	$\frac{5+6+3}{2}=7$	6	1

Note: The lone pair of $\mathbf{[SbCl_6]^{3-}}$ is steriochemically inactive and that of $\mathbf{XeF_6}$, is boderline of stereochemically active and stereochemically inactive condition.

34. Correct option is (d)

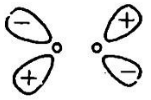
C_2 = valence electron = 12

$C_2 = \sigma_{1s}^2\ \sigma_{1s*}^2\ \sigma_{2s}^2\ \sigma_{2s*}^2\ \pi_{2p}^4$

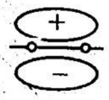


y < σ_{2px}

π^* = gerade while π = ungerade



π^*
(gerade)



(u)
(ungerade)

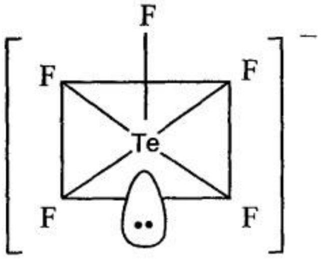
Centre of symmetry No centre of symmetry

36. Correct option is (b)

$[TeF_5]^{-1} = \frac{4>E>?}{7} = 6$

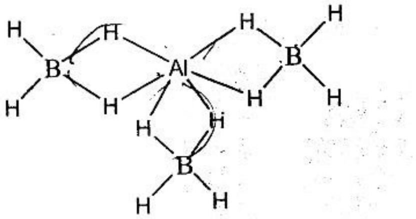
Number of lone pair = 1

Structure is square pyramidal



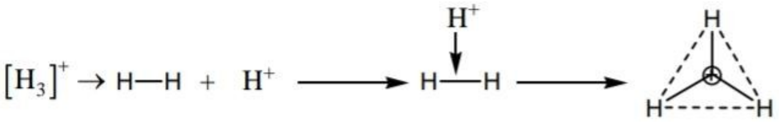
37. Correct option is (c)

The structure of $[Al(BH_4)_3]$ is



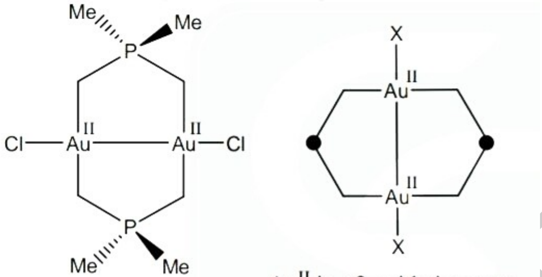
Thus, number of 3c-2e bond is equal =6

38. Correct option is (c)



Each bond angle is 60°

39. Correct option is (c)

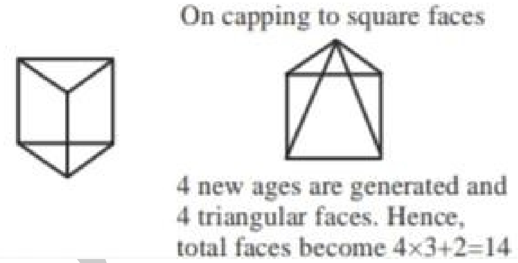


Au^{II} in +2 oxidating state

Oxidation state of gold in this complex is 2

40. Correct option is (a)

Number of triangular anti-prism are 8 , in icosahedron it is 20 and in tricapped trigonal prism (capped on square faces) it is 14

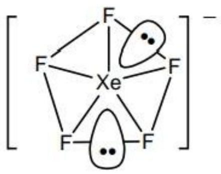


On capping to square faces

4 new ages are generated and 4 triangular faces. Hence, total faces become 4×3+2=14

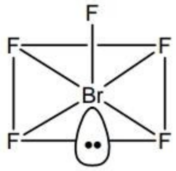
41. Correct option is (a)

$[XeF_5]^- \Longrightarrow$



Shape = Pentagonal planar

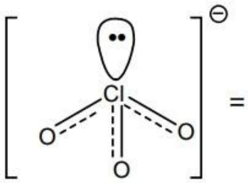
$[BrF_5] \Longrightarrow$



Shape = square pyramidal

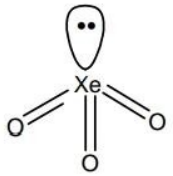
42. Correct option is (a)

$ClO_3^- = \frac{;>4\times G>?}{H} = \frac{74}{H}$ = 3+1 =4 sp^3 (Tetrahedral)



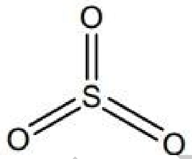
= Pyramidal shape

Xe= $\frac{H>4\times 7}{H} = \frac{74}{H}$ =3+1=4→sp^3 (Tetrahedral)



= Pyramidal shape

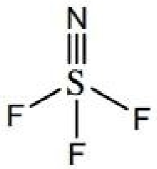
$SO_3 = \frac{4>4\times G}{H} = \frac{76}{H}$ =3→sp^2 (Trigonal planar)



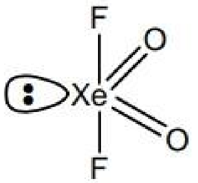
43. Correct option is (d)

$SNF_3 = \frac{4>E>;\times G}{H} = \frac{G7}{H} = 4 = sp^3 = Td$

$XeO_2F_2 = = \frac{H>4\times 7>;\times 7}{H} == \frac{G6}{H}$ =4+1= 5=sp^3d→TBP



Tetrahedral



Trigonal bipyramidal

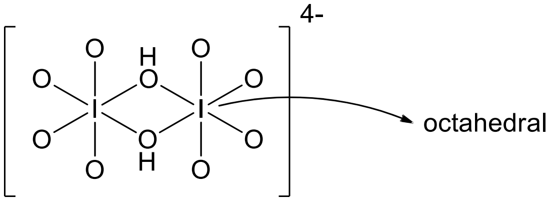
44. Correct option is (a)
According to Bent's Rule, 'more electro negative element occupy axial position in trigonal bipyramidal geometry.

45. Correct option is (b)
According to Allred-Rochow, electronegativity can be given as

$$X = \frac{0.3590 Z_{\text{NOO}}}{\text{r}^7} + 0.744$$

where r^2 = covalent radius.

46. Correct option is (a)
The correct structure of dinuclear anion $[I_2(OH)_2O_8]^{-4}$ with two bridging oxo groups, is as shown below

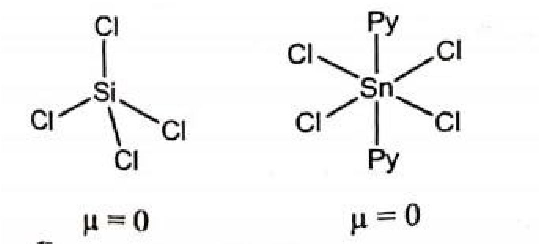


47. Correct option is (b)
According to MOT
NO→ $\sigma^2_{1s} < \sigma^2_{1s*} < \sigma^2_{2s} < \sigma^2_{2s}* < \pi^2_{2px} = \pi^2_{2py} < \sigma^2_{2pz} < \pi^1*_{2pz} = \pi*_{2py} < \sigma_{2pz}*$
Bond order of NO = $\frac{10 - 5}{2} = 2.5$
Bond order of $NO^+ = \frac{10 - 4}{2} = 3$
Hence, as bond order increases v (NO^+) increases and NO^+ → EPR inactive as no unpaired electron
In NO^+ HOMO is σ_{2pz} that is close to more electronegative atom (Oxygen).

48. Correct option is (c)
The energy difference between π* and σ* is very small and it absorbs at λ_{max} =520 nm. When I_2 is dissolved in a non-donor solvent, there is no effect on energies of π* and σ* of I_2 and it absorbs at λ_{max} =520 nm. Interaction of solvent donor orbital with the σ* ,I_2 LUMO result in a lower occupied bonding orbital and a higher uncoupled bonding orbital As a result the π*→ σ* transition for the I_2 donor adduct is shifted higher in a energy and lower wavelength.
Hence, electron donor < weak donor < strong donor

49. Correct option is (d)
(i) The electronegativity of CF_3 is less than NF_2
(ii) NH_2 group has less electronegative than NF_2
(iii) OH group has less electronegative than NF_2
(iv) CH_3 and C_2H_5 group have almost similar value of electronegativity.

50. Correct option is (c)



51. Correct option is (c)

According to MOT the LUMO of CN^- and O_2 respectively are $\boldsymbol{\pi_g}$ **and** $\boldsymbol{\sigma_u}$

52. Correct option is (a)

As bond order increases, stretching frequency increases.

$O_2^+ = 2.5$, $O_2 = 2$, $O_2^- = 1.5$ $O_2^{+2} = 1$

53. Correct option is (b)

$\mathbf{O_2^-} \rightarrow \sigma^2_{1s} < \sigma^2_{1s*} < \sigma^2_{2s} < \sigma^2_{2s}* < \pi^2_{2px} = \pi^2_{2py} < \sigma^2_{2pz} < \pi^2*_{2px} = \pi^1*_{2py}$

$\mathbf{O_2} \rightarrow \sigma^2_{1s} < \sigma^2_{1s*} < \sigma^2_{2s} < \sigma^2_{2s}* < \pi^2_{2px} = \pi^2_{2py} < \sigma^2_{2pz} < \pi^1*_{2px} = \pi^1*_{2py}$

Bond order of $\mathbf{O_2^-} = \frac{6-3}{2} = 1.5$

Bond order of $\mathbf{O_2} = \frac{6-2}{2} = 2$

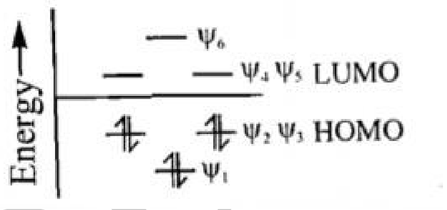
Bond order of O_2 is more than O_2^- thus, bond length of O_2^- is more than O_2.

- The superoxide ion O_2^- is able to abstract proton from weak acids. It reacts with a proton or proton donor to form HO_2

  $O_2^- + HX \rightarrow HO_2 + X^-$
- The superoxide ion O_2^- is a stronger oxidising agent than O_2
- O_2^- does not possess dipole moment thus, it is IR inactive.

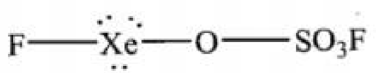
54. Correct option is (d)

The MO diagram of benzene is

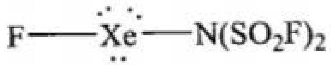


Thus both HOMO and LUMO are doubly degenerate.

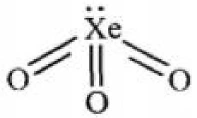
55. Correct option is (a)



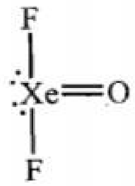
Geometry = TBP
Linear shape



Geometry = TBP
Linear shape



Geometry = Tetrahedral
Pyramidal shape



Geometry = TBP
T– shaped

56. Correct option is (a)

The bond order can be calculated by molecular orbital theory

Molecule	Bond Order
NO^+	3
O_2^+	2.5
N_2^+	2.5
C_2^+	1.5

$NO^+ = \sigma^2_{1s} < \sigma^2_{1s*} < \sigma^2_{2s} < \sigma^2_{2s}* < \pi^2_{2px} = \pi^2_{2py} < \sigma^2_{2pz}$

$O_2^+ = \sigma^2_{1s} < \sigma^2_{1s*} < \sigma^2_{2s} < \sigma^2_{2s}* < \pi^2_{2px} = \pi^2_{2py} < \sigma^2_{2pz} < \pi^1*_{2pz} = \pi^1*_{2py}$

$N_2^+ = \sigma^2_{1s} < \sigma^2_{1s*} < \sigma^2_{2s} < \sigma^2_{2s}* < \pi^2_{2px} = \pi^2_{2py} < \sigma^1_{2pz}$

$C_2^+ = \sigma^2_{1s} < \sigma^2_{1s*} < \sigma^2_{2s} < \sigma^2_{2s}* < \pi^2_{2px} = \pi^1_{2py}$

Bond order of $NO^+ = \frac{8-2}{2} = 3$

Bond order of $O_2^+ = \frac{8-3}{2} = 2.5$

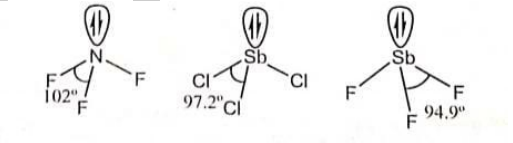
Bond order of $N_2^+ = \frac{7-2}{2} = 2.5$

Bond order of $C_2^+ = \frac{5-2}{2} = 1.5$

57. Correct option is (d)

According to VSEPR theory as the size of central atom increases bond angle decreases. Hence, Bond angle of $NF_3 > SbCl_3$,SbF_3

Now, in between $SbCl_3$ and SbF_3 . 'F' is more electronegative and pull the bond pair towards itself due to which bond angle FSbF decreases. The experimental bond angles are



58. Correct option is (c)

•VSEPR theory is applicable for main group elements not for transition metal elements. Hence $\mathbf{[PtCl_4]^{2-}}$ can't be explained.

•Also VSEPR theory can not explain the structure of molecules which have stereochemically inactive lone pair. In $[TeCl_6]^{-2}$ there is one such lone pair. It is perfectly octahedral and hence can't be described by VSEPR theory.

•PF_3 is having lone pair and is trigonal pyramidal according to VSEPR theory. And SF_6 is perfectly octahedral having no lone pair on 'S'.

59. Correct option is (b)

In B_2 and C_2 , s-p mixing takes place thus, energy of $2\sigma_g$ is greater than $1\pi_u$ whereas there is no s-p mixing takes place in O_2, thus, energy of $2\sigma_g$, is less than that of $1\pi_u$

60. Correct option is (c)

SO_3^{2-}

Valence electrons = 6

6 – 2 – 2 = 2

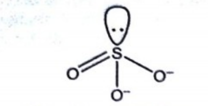
↓ ↓ ↓

1σ 2σ [one

1π $2O^-$ lone

1O pair]

Hybridisation=1+2+1 = 4 i.e. sp^3



Trigonal pyramidal shape

Shape = Trigonal pyramidal

BrF_4^-

Valence electrons = 7

$7 – 3 = 4 + F^-$

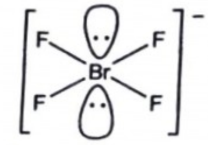
↓ ↓ ↓

3σ [Two [One

3F lone coordinate

Pair] bond]

Hybridisation = 3 + 2 + 1 = 6 i.e. sp^3d^2



Square planar shape

CO_3^{2-}

Valence electrons = 4

4 - 2 - 2 = 0

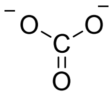
↓ ↓

1σ 2σ

1π $2O^-$

1O

Hybridisation = 1 + 2 = 3 i.e. sp^2



Shape = Trigonal planar

61. Correct option is (a)

Allred-Rochow electronegativity (**χAR**):

χAR = $(3590\, z^*/r^2) + 0.744$

where, r = covalent radius (in pm), z* =effective nuclear charge

62. Correct option is (c)

Firstly draw the molecular orbitals. Then add electrons and count the number of bonding and anti bonding electrons.

The bond order of a bond is half the difference between the number of bonding and antibonding electrons.

Bond order = 1/2 [Bonding-Anti-bonding]

The C-C sigma bonds.

Each C-C σ bond is a localised. It has 2 bonding electrons and zero non-bonding electrons.

σ Bond order = ½ (B-A) = ½ (2-0) = 1

The C-C π bond.

Benzene has 6 molecular π -orbitals of these, three are bonding and three are anti-bonding. The six π -electrons go into the three bonding orbitals.

π Bond order= ½ (B-A) = ½ (6-0) = 3

This is the π bond order for 6 C-C bonds for one C-C π bond, Bond order = 3/6 =0.5

For a single C-C bond in Benzene, the total Bond Order σ + π = 1+ 0.5 =1.5

63. Correct option (c)

Applying VSEPR theory we can easily find out structures of the molecules

BrF_3 has 3 bond pairs and 2 lone pairs, hence it's geometry is TBP but structure is T-shaped

$FClO_2$ has 3 bond pairs and 1 lone pair, hence its geometry is Tetrahedral but structure is pyramidal.

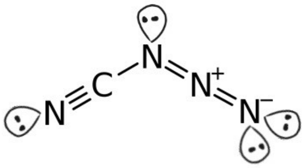
$[XeF_5]^-$ has 5 bond pair and 2 lone pairs, hence its geometry is Pentagonal bipyramidal but structure is pentagonal plannar.

$[ClF_4]^-$ has 4 bond pairs and 2 lone pairs, hence its geometry is Octahedral but structure is square plannar.

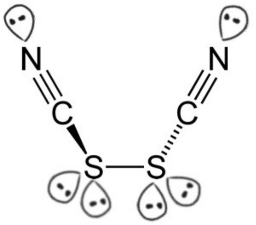
XeO_3 has 3 bond pairs and 1 lone pair, hence its geometry is Tetrahedral but structure is pyramidal.

64. Correct option (a)

The molecular structure are as follows



cyanogen azide



thio cyanogen

65. Correct option (a)

Electronic configuration of Hg = $5d^{10}\ 6s^{2}$

For $Hg^{+} = 5d^{10}\ 6s^{1}$

In order to form $[Hg_2]^{2+}$ there will be one sigma bond between two Hg^{+} atoms.

8

Acids and Bases

Hints & Solutions

1. Correct answer is (b).

Higher the charge and smaller size of the central metal cation increases the acidic strength of hydrated complex because it polarizes O-H band of H_2O easily.

In $[Sc(H_2O)_6]^{+3}$, Sc is in +3 oxidation state and has smallest size.

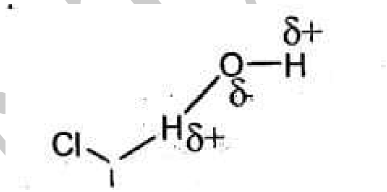
Therefore, in size of depositive ions increase in the order

$[Sc(H^2O)_6]^{+3} > [Ni(H_2O)_6]^{+2} > [Mn(H_2O)_6]^{+2} > [Na(H_2O)_6]^{+}$

2. Correct answer is (b).

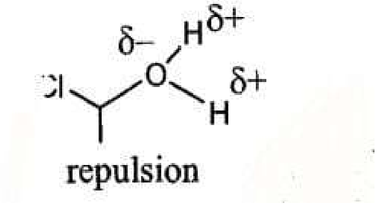
$nH_2O + Cl^- \rightarrow [Cl(H_2O)n]^-$

If negative end of O-H dipole approaches the Cl^- ion, then there will be repulsion.



ion dipole interaction positive and of OH dipole approaches the Cl^- ion and form $Cl(H_2O)n]^-$

Not stabilized. Thus H_2O does not behave as a base $6H_2O + Mg^{+2} \rightarrow [Mg(H_2O)_6]^{+2}$



In this reaction Mg^{+2} behave as lewis acid and H_2O behave as a ligand or lewis base.

3. Correct answer is (b).

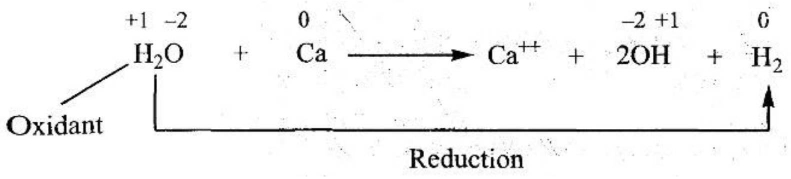
4. Correct answer is (c)
$CH_3COOH + C_5H_5N: \rightarrow CH_3COO^- + C_5H_5NH^+$ (solvo cation)
$CH_3COOH + H_2SO_4 \rightarrow CH_3COOH_2^+ + HSO_4^-$ (solvent anion)
$HClO_4 + H_2SO_4 \rightarrow ClO_4^- + H_3SO_4^+$ (solvent cation)→ [weak acid]
$SbF_5 + 2HF \rightarrow [SbF_6] + H_2F^+ \rightarrow$[strong acid]

5. Correct answer is (c)
$HClO_4$ behave as an acid in **H_2SO_4**, because **$HClO_4$** contain higher dissociation constant than that of **H_2SO_4**.
$HClO_4$, pK_a, value -9
H_2SO_4 , pK_a value -3,
HNO_3 , pK_a value -1,
CH_3COOH , pK_a value 4.7.
pK_a value of **$HClO_4$** > pK_a value of **H_2SO_4**

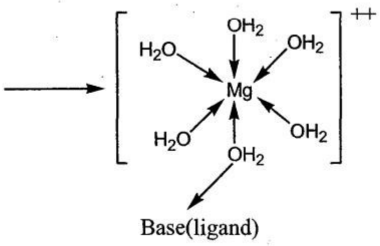
6. Correct answer is (d)
For aqua ion complex , acidity is more when (i) small size
(ii) greater charge.

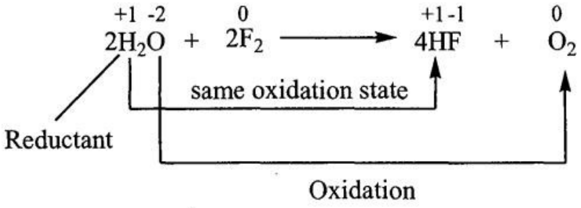
7. Correct option is (b)
(I) $2[Fe(CN)_6]^{3-} + H_2O_2 + OH^- \rightarrow 2[Fe(CN)_6]^{4-} + 2H_2O + O_2$
(alkaline medium) Reduction
(II) $2[Fe(CN)_6]^{4-} + 2H^+ + H_2O_2 \rightarrow 2[Fe(CN)_6]^{3-} + 2H_2O$
(acidic medium) Oxidation
(III) $2MnO_4^- + 6H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$
(acidic medium) Reduction

8. Correct option is (a)
In reaction (i)Water acting as an oxidant oxidizing Ca to Ca^{+2} getting itself reduced to H_2.
In reaction (ii) Water act as Lewis acid accepting elecron from Cl^- which act as a ligand.
In reaction (iii) Water act as Lewis base donating electron to Mg^{+2} .
In reaction (iv) Water acting as an redutant reducing F to F^-.

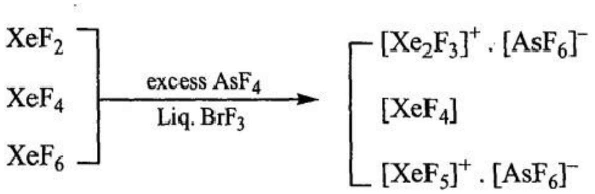


i) $H_2O + Cl^{-1} = [Cl(H_2O)n]^{-1}$
Where, Cl = Base, H_2O = Acid
iii) $6H_2O + Mg^{+2}$ → octahedral complex shown below





9. Correct option is (c)



Separation of XeF_4 from a mixture involves preferential complexation of XeF_2 and XeF_6 and XeF_4 is then removed in vacuum

10. Correct option is (b)

(A) NOCl +Sn $\xrightarrow{N2O4}$ $[NO]^+ + Cl^-$ ($[NO]^+$ is not majore product)
(B) NOCl+ $AgNO_3$ → $AgCl + N_2O_4$ (Neutralization reaction)
(C) NOCl +BrF_3→ $[NO]^+ + BrF_4^-$
(D) NOCl+ $SbCl_5$ → $[NO]^+ + SbCl_6^-$

11. Correct option is (a)

$KF + BrF_3 \rightarrow K^+ + BrF_4^-$
$SnF_4 + 2BrF_3 \rightarrow 2[BF]^+ + [SnF_6]^{-2}$
$SbF_5 + BrF_3 \rightarrow BrF_2^+ + [SbF_6]^-$
This only KF increases the concentration of BrF_4^- in BrF_3.

12. Correct option is (c)

Due to more acidity of HCl it will undergo more ionization. Hence, concentration of **Cl^-** will be maximum.

13. Correct option is (d)

Cl_2 → solvolysis and disproportionation of Cl_2 in NH_3
$Cl_2 + 2NH_3 \rightarrow NH_2Cl + NH_4^+ + Cl^-$
S_8 → undergoes disproportionation in liquid NH_3
$5S_8 + 16NH_3 \rightarrow 4SN^- + 4\,\mathbf{S_6^{(2}} + 12NH_4^+$
CH_3COOH acts as strong acid in NH_3
$CH_3COOH + NH_3 \rightarrow CH_3COO^- + NH_4^+$
Molecules that do not behave as acid in water, may behave as weak acids in NH_3
$H_2NCONH_2 + NH_3 \rightarrow NH_4^+ + NH_2CONH^-$

14. Correct option is (d)

$AsF_5 + 2HF \rightarrow [AsF_6]^- + [H_2F]^+$
$PF_5 + 2HF \rightarrow [PF_6]^- + [H_2F]^+$
$BF_3 + 2HF \rightarrow [BF_4]^- + [H_2F]^+$
$BrF_3 + HF \rightarrow [BrF_2]^+ + [HF_2]^-$
BrF_3 acts as base as it donate F^- in HF

15. Correct option is (d)

$SbF_5 + Br \rightarrow [BrF_2]^+ + [SbF_6]^-$ →Lewis base behaviour of BrF_3
$[BrF_2][SbF_6] + Ag[BrF_4] \rightarrow Ag[SbF_6] + 2BrF_3$→Neutralization
$KF + BrF_3 \rightarrow K^+ + [BrF_4]^-$ → Lewis acid behaviour of BrF_3
$2BrF_3 \rightarrow [BrF_2]^+ + [BrF_4]^-$ → self-ionization

16. Correct option is (d)

$A \rightarrow Cl_2 + 2H_2O \rightarrow HOCl + H_3O^+ + Cl^-$
$B \rightarrow Cl_2 + 2NH_3 \rightarrow NH_4Cl + NH_4^+ + Cl^-$
Above both reactions are example of solvolysis as well as disproportionation.

17. Correct option is (b)

$MnO_4^- + e^- \rightarrow MnO_4^{-2}$ (By Na in liq. NH_3)
$Me_3CH \rightarrow Me_3C^+$ (By super acids, only super acids attack C-H bond)
$Ag + Au \rightarrow Ag[AuF_4]$
$H_3PO_4 + H^+ \rightarrow P(OH)_4^+$
(This reaction occurs in H_2SO_4 because in H_2SO_4 solvent, H_3PO_4 acts as a base)

18. Correct option is (b)

SbF_5 is strongest acid and PH_3 is strongest base.

19. Correct option is (a)

$IO_3^-\,(aq) + 5I^-(aq) + 6H^+\,(aq) \rightarrow 3I_2(aq) + 3H_2O(l)$

20. Correct option is (a)

•When aqueous solution of $AgNO_3$ is added to an aqueous solution of KCl, white ppt of AgCl is formed.

$KCl + AgNO_3 \rightarrow \underset{\text{White ppt}}{AgCl} + KNO_3$

But in liquid NH_3, the direction of the reaction is reversed.

$AgCl + KNO_3 \rightarrow KCl + AgNO_3$

• $NH_4Br + KNH_2 \rightarrow KBr + 2NH_3$

This reaction is neutralization reaction in liquid NH_3

Ammonia solutions of alkali metals and alkaline earth metals are strong reducing agents.

$Fe(CO)_5 + 2e^- \rightarrow [Fe(CO)_4]^{-2} + CO$

21. Correct option is (c)

$2BrF_3 + SnF_4 \rightarrow (BrF_2)_2[SnF_6]$

Species formed in reaction are BrF_2^+ and $[SnF_6]^{-2}$

$AuF_3 + BrF_3 \rightarrow BrF_2^+[AuF_4]^-$

Species formed in reaction are BrF_2^+ and $[AuF_4]^-$

22. Correct option is (d)

This can be explained with the help of HSAB principle.

•Be^{+2} is hard acid hence favour hard base F^-

•Also La^{+3} is hard acid, thus favour hard base CO_3^{-2} . Therefore, process B and D are not feasible.

$\mathbf{La_2(CO_3)_3 + Bi_2S_3 \overset{gives}{\leftrightarrow} La_2S_3 + Bi_2(CO_3)_3}$

HA HB ← HA SB

$\mathbf{BeF_2 + HgI_2 \overset{gives}{\longleftrightarrow} BeI_2 + HgF_2}$

HA HB ← HA SB

23. Correct option is (d)

$HOSO_2F + HF \rightarrow [H_2F]^+ + [SO_3F]^-$

Acid

$CH_3CO_2H + 2HF \rightarrow [CH_3C(OH)_2]^+ + [HF_2]^-$

Base

$LiF + HF \rightarrow Li^+ [HF_2]^-$

(Base)

$H_2O + HF \rightarrow H_3O^+ + F^-$

(base)

24. Correct option (d)

In first reaction, Xe is acting as electron donor to become $[Xe]^+$, hence as a base.

In second reaction XeF_4 is accepting electron to become $[XeF_4]^-$, hence it is an acid.

25. Correct option (a)

Lewis acidity of silicon halides depends on electronegativity of halide groups

$$lewis\ \ acidity\ \ of\ SiX \propto Electronegativity\ \ of\ \ X$$

since, electronegativity order is F > Cl > Br > I , thus correct order of lewis acidity is $\boldsymbol{SiI_4}$ < $\boldsymbol{SiBr_4}$ < $\boldsymbol{SiCl_4}$ < $\boldsymbol{SiF_4}$. Hence Statement (i) is correct.

In statement (ii) $SnCl_2$ is given, which is a Hypovalent compound, having incomplete octet and hence will behave as Lewis Acid.

Aluminosilicates have general formula AlM_xSiO_y since there is NO H^+ ion present thus there is no chance of Brönsted acidity.

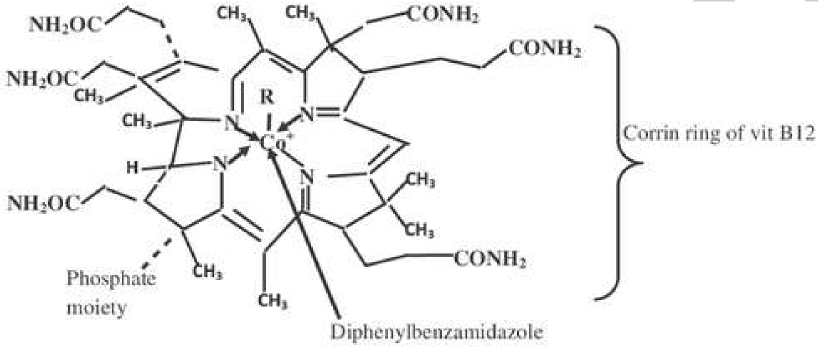
9

Bioinorganic Chemistry

Hints & Solutions

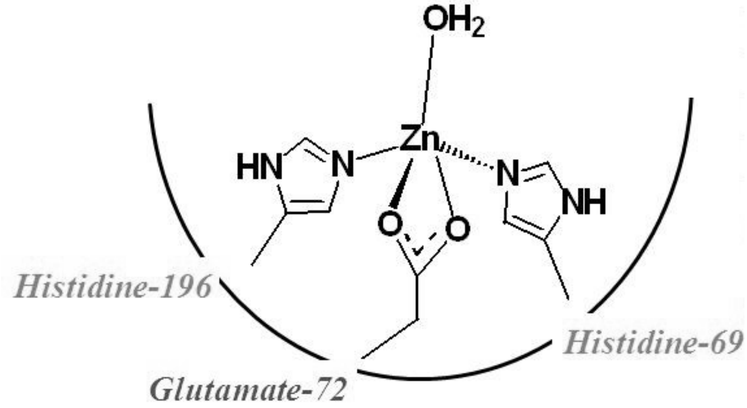
1. Correct Option (b)

Vitamin B_{12} molecule is built-around a Corrin ring containing cobalt (III) atom.

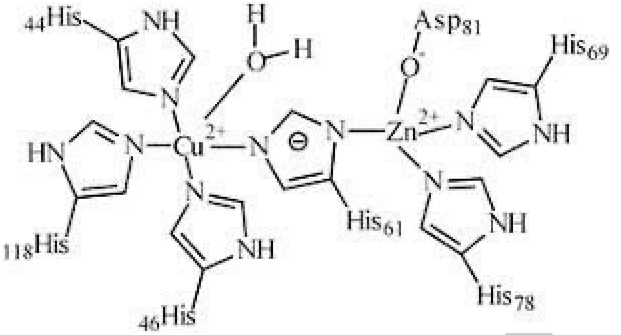


2. Correct answer: (b)

Carboxypeptidase enzyme contains Zn^{+2} ion and it cleaves (hydrolyses) the carboxy terminal amino acid from a peptide chain.

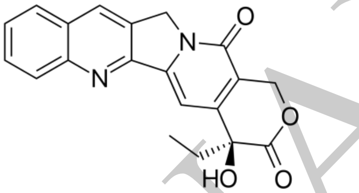


3. Correct answer is (b)



4. Correct answer is (c).

Camptothecin, an quinolone alkaloid, is used as a chemotherapeutic agent in the treatment of leukemia



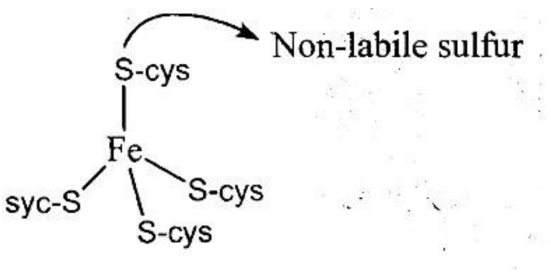
5. Correct answer is (d)

$N_2 + 8H^+ + 8e^- + 16\ ATP \rightarrow 2NH_3 + H_2 + 16ADP + 16Pi$

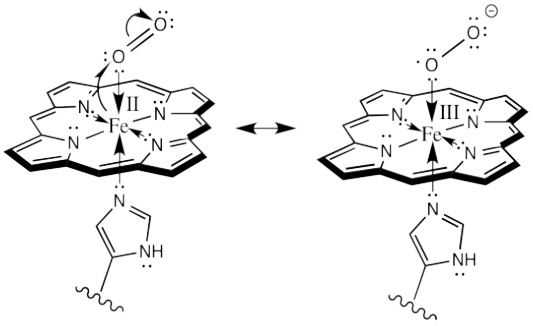
6. Correct answer is (c).

EPR studies show that, Mn^{2+} can replace Mg^{2+} in nucleic acid processing enzymes

7. Correct answer is (d).

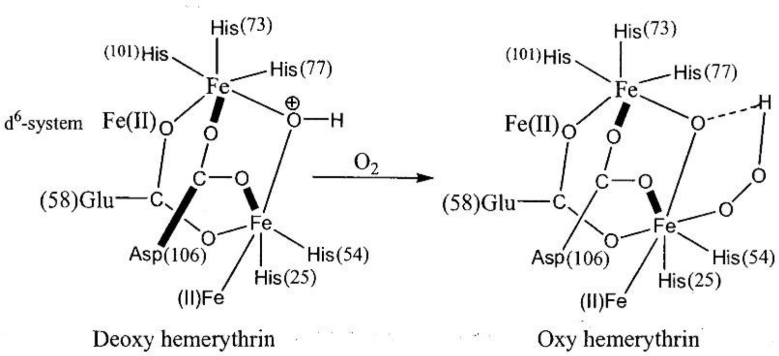


8. Correct answer is (a).



Hemoglobin

9. Correct answer is (a).



10. Correct answer is (c).

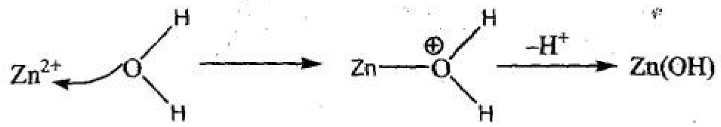
NAD$^+$←Biological reductant
↓
Flovoprotein
↓
cyt b→ cyt bf → PC

11. Correct answer is (a).

Fe= Hb & Mb cytochromes
Mo= nitrogen fixation
Cu= hemocyanin

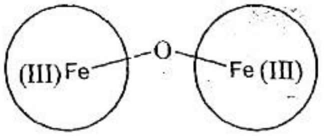
Zn= metalloezymes

12. Correct answer is (b)
Because zinc is a Lewis acid and hence,



So, correct option is (b)
However, oxidase are enzyme that catalyse the reduction of $O_2 \rightarrow H_2O$ or H_2O_2 .
$O_2(g) + 4e^- + 8H^+$ (inside) $\rightarrow 2H_2O(l) + 4H^+$ (outside)

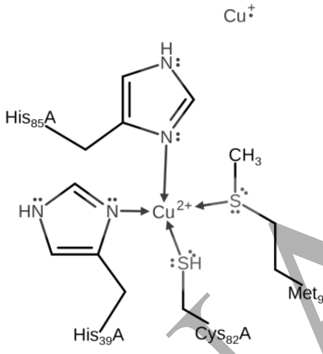
13. Correct answer is (b)
Free heme (i.e. without globular protein chain) it foms μ -oxodimer) i.e.



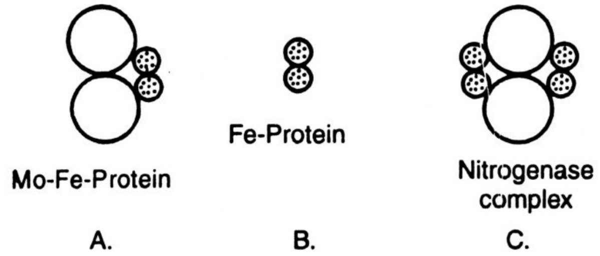
μ-oxo-dimer (hematin).

which is unable to bind O_2

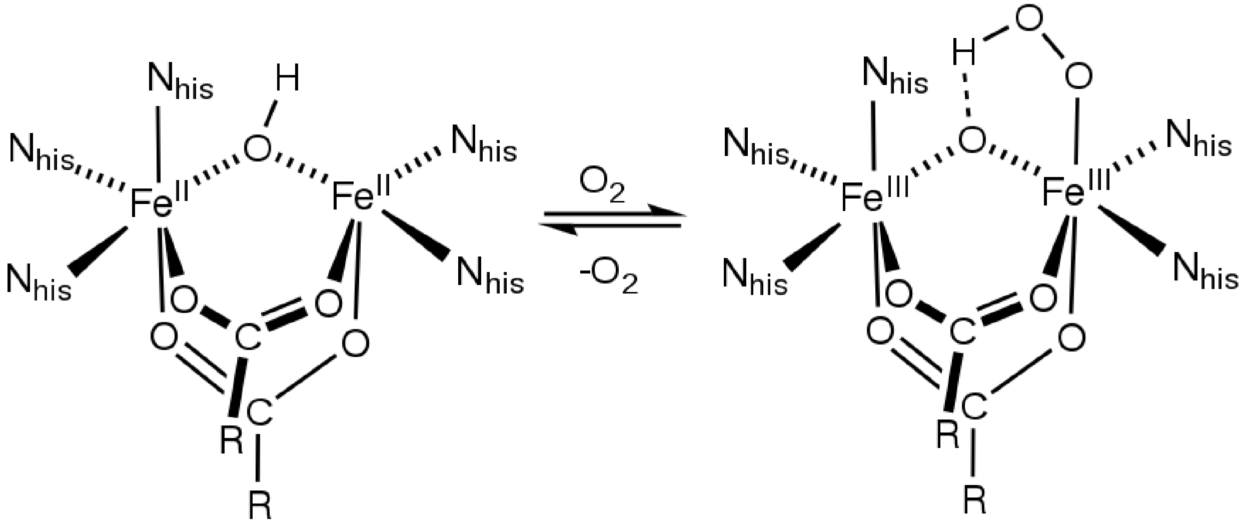
14. Correct answer is (d)
The coordination geometry of copper (II) in the type I copper protein plastocyanin is distorted tetrahedral



15. Correct answer is (a)
Nitrogenase enzyme cofactor contains Fe, Mo also known as Iron-molebdenum cofactor.



16. Correct answer is (b)



Hemerythrin, one iron centre is penta coordinated and other is hexacoordinated and iron exist at peractive site found in marine invertebrates.

17. Correct answer is (c)

Wilson's disease is caused by excess accumulation of Cu in the body. Thus the reason being low level of copper-storage protein, ceruloplasmin.

18. Correct answer is (d)

Prolonged use of $ZnSO_4$, for the cure of Zn deficiency, reduces the amount of copper, iron and calcium levels in body.

19. Correct answer is (b)

l-DOPA, also known as levodopa and l-3,4-dihydroxyphenylalanine, it crosses the protective blood-brain barrier, whereas dopamine itself cannot. Thus, l-DOPA is used to
increase dopamine concentrations in the treatment of Parkinson's disease and dopamine-responsive dystonia.

20. Correct answer is (a)

Catalase is a tetramer of four polypeptide chains covering 500 amino acids.
It works as H_2O_2+ Fe (III)-E $\rightarrow H_2O$+O=Fe (IV) - E
H_2O_2+O= Fe(IV) – $E^+ \rightarrow H_2O$ + Fe(III)-E + O_2
The colour arises as Fe(III) changes into Fe(IV).

21. Correct answer is (b)

The chemical reaction involved is shown below**:**
$N_2 + 8H^+ + 8e^- + 16\ ATP \rightarrow 2NH_3 + H_2 + 16ADP + 16Pi$

22. Correct answer is (c)

Ozone is a diamagnetic gas which is of dark blue coloured due to absorption of red light.
(λ=557 and 602 nm)

Ozone depletion discovered by J.C. Farman over Halley Bay in Antarctica.
Ozone also show strong absorption in λ =255 UV which is good for earth, it act as a green house , sunlight can come in but it can not go out .
'UV-b' is most dangerous, would damage the DNA of all living beings.
Ozone protects earth by keeping it warm .

23. Correct answer is (d)

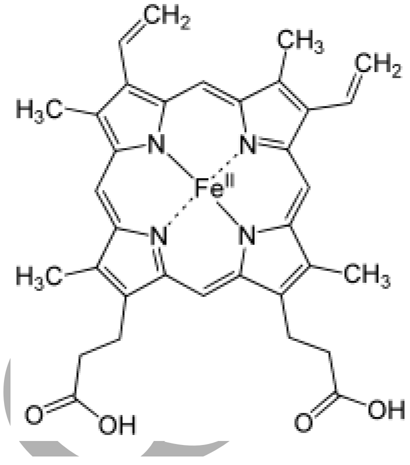
Molybdoenzymes containing Molybdenum as the central metal, since it exists in two stable oxidation states (IV) and (VI), thus it can transfer oxygen atom to substrate as well as it can abstract oxygen atom from the substrate.

24. Correct answer is (a)

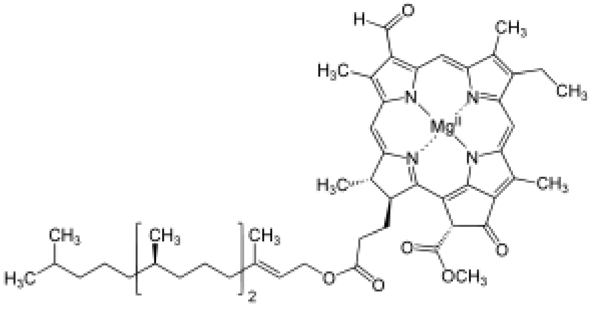
The movement of iron atom and imidazole side chain of histidine toward the porphyrin plane results in breaking of some of the salt bridges. The breaking of these salt bridges reduces the strain in hemoglobin molecule. Therefore, the oxyform of hemoglobin is called relaxed state (i.e., R state). The T form of deoxyhemoglobin discourages the addition of first dioxygen molecule.
The bonding of one dioxygen molecule to a subunit of hemoglobin reduces the steric hindrance in the other subunits (due to breaking of salt bridges) and therefore encourages the third as well as fourth subunits. This is called cooperative mechanism

25. Correct answer is (a)

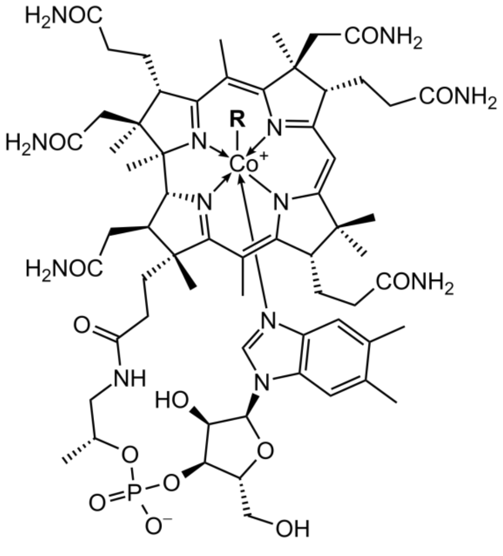
Total number of π-electrons in microcyclic rings of heme, coenzyme B_{12} and chlorophyll is
Heme=11 π electrons in microcyclic ring
Coenzyme B_{12}= 5 π electrons in microcyclic ring
Chlorophyll= 10 π electrons in microcyclic ring
Check-out below images.



HEME, 11 π electrons in microcyclic ring



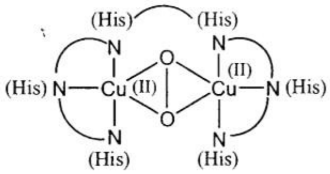
Chlorophyll, 10 π electrons in microcyclic ring



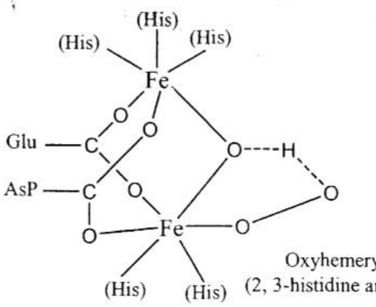
R = 5'-deoxyadenosyl, CH_3, OH, CN

Vitamin B_{12}, 5 π electrons in microcyclic ring

26. Correct option (b)



Oxyhemocyanin
(3, 3-histidine amino acids)



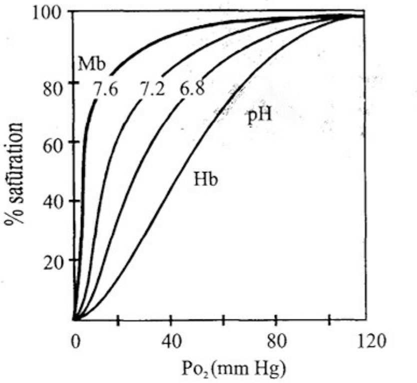
Oxyhemerythrin
(2, 3-histidine amino acids)

27. Correct answer is (d)

In 1956, in Japan minamata disater had been broken out in coastal area. This is a neurological syndrome caused by mercury pollution. The Hg^{+2} get converted into $MeHg^{+}$ by carbonic biomethylation. Which form strong bonding with thiol(-SH) group of protein having cysteine amino acid. Hence, A, B and C are correct.

28. Correct answer is (a)

Myoglobin is pH independent .



Lungs (gills) Hb+ $4O_2$ → $(HbO_2)_4$

Tissues $Hb(O_2)_4$ +4Mb → $4MbO_2$ + Hb pH dependent shown by hemoglobin is known as Bohr effect (binds one H^+ for every dioxygen molecules)

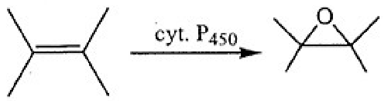
29. Correct answer is (a)

Oxyhemocyanin stables as oxygen carrier.

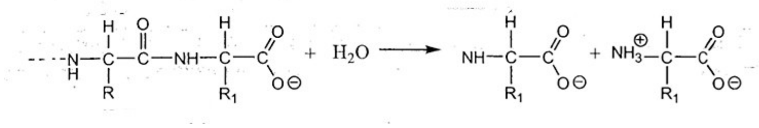
Carbonic anhydrase

Carbonic anhydrase converts CO_2 to H_2CO_3

Cytochrome P_{450} oxidizes alkene to epoxide.



Carboxy peptidase A catalyzes the hydrolysis of C-terminal peptide bond.



30. Correct option is (a)

The carbonic anhydrase enzyme that catalyst the rapid interconversion of carbon-dioxide and water to bicarbonate and protons (and vice versa).

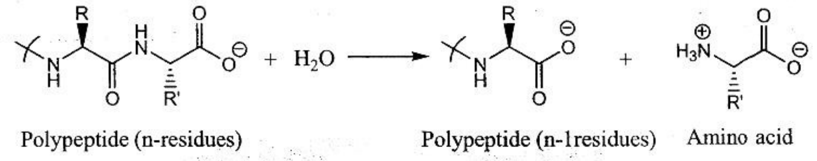
$CO_2+H_2O \rightarrow H_2CO_3$ (in tissue high CO_2 concentration)

$HCO_3^- + H^+ \rightarrow H_2CO_3 \rightarrow \rightarrow CO_2 + H_2O$ (in lungs and nephronse of kidney)

Hydration occur in blood at high pH values.

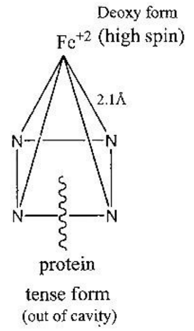
Dehydration occur in lungs at low pH values.

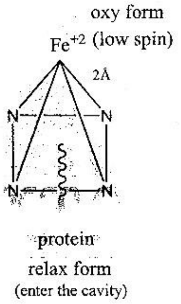
Carboxypeptidase A is a pancreatic exopeptidase that hydrolise peptide bond of C terminal.



Where, R =Arg, Lys, and Ornithine

31. Correct answer is (a)



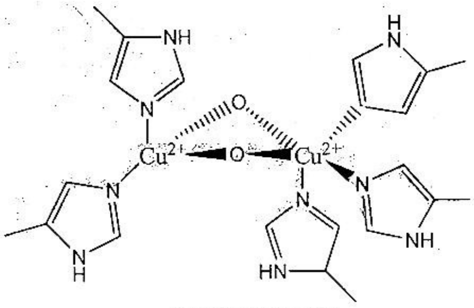


Deoxy . Hb	**Oxy Hb**
Fe^{+2} HS	Fe^{+2} LS

$t_{2g}^4\, e_g^2$	$t_{2g}^6\, e_g^0$
Fe is above the plane which tends to increase the Fe-N distance .	Fe is fitted well inside the plane thus reducing Fe-N bond distance.

32. Correct option is (a)

Oxy-hemocyanin are proteins that transport oxygen throughout the bodies of some invertebrate animals. These metalloprotein contain two copper atoms that reversibly bind a single oxygen molecule (O_2). The total of six coordinated imidazole units of histidine present in the active site of oxy-hemocyanine.

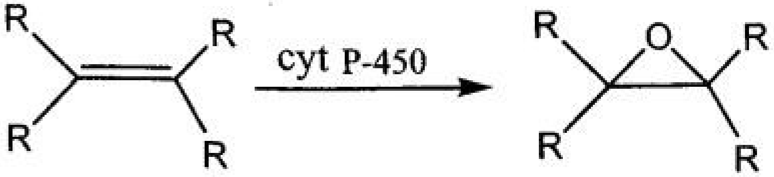


Oxy-hemocyanin

33. Correct option is (a)

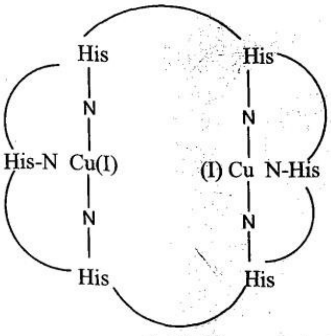
Myoglobin is found in tissue and store the oxygen in tissue transported by Haemoglobin ,it contain high-spin five coordinate Fe(II), reacts readily & reversibly with O_2 to produce a low-spin Fe(II)-O2 complex [storage of O_2]

Cytochrome P_{450} haem containing monooxygenases, catalyses the insertion of oxygen in substrate , oxidation of 5-exoposition of camphor, oxidation of alkene etc.



34. Correct option is (b).

In deoxyhaemocyanin Cu is in Cu(I) state i.e. have $d^{10}s^0$ configuration therefore it colourless and diamagnetic. Diamagnetism is due absence of unpaired electrons and colourless is due to no d-d transition as all the orbitals are filled.



Cu(I) d^{10}

35. Correct option is (d).

O_2 in free state, $\nu_{()(}$ = 1580 cm^{-1} when O_2 bound to hemoglobin, it makes strong coordinate bond with Fe of hemoglobin and O-O bond strength decreases slightly, so in oxy-hemoglobin, $\nu_{()(}$ = 1100 cm^{-1}.

36. Correct option is (a).

Hemoglobin - O_2 trasnport & iron
Cytochrome b- Electron carrier & iron
Vitamin B_{12}- Group transfer reactions & cobalt
Hemocyanin - O_2 transport & copper

37. Correct option is (a)

Absence of globin chain following reaction is occur

$$PFe^{II} + O_2 \rightarrow PFe^{II}\text{-}O_2 + Fe^{II}P \rightarrow P\text{-}Fe^{III}\text{-}O\text{-}O\text{-}Fe^{III}\text{-}P$$

$$\xleftrightarrow[\text{reversible}]{} 2PFe^{IV}{=}O \xrightarrow{234} \overset{(66)}{P}Fe^{III}\text{-}O\text{-}Fe^{III}\text{-}P$$

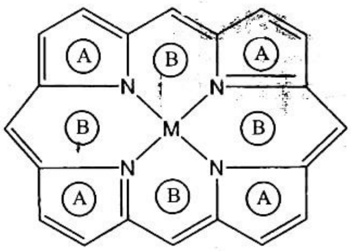
(Haematin)

38. Correct option is (c)

Pt- complex used as anticancer drug
Au-complex used as anti arthritis agent
Gd-complex used in MRI as contrast agent due to their strong paramagnetic behaviour
Li-complex used in Maniac depression

39. Correct option is (a)

Structure of m-porphyrine complex can be shown as



Here, (A) represents = five membered ring
(B) represents = six membered ring.
Thus, these are four 5-membered ring and four-6-membered ring.

40. Correct option is (a)

cis-platin modifies the DNA structure by binding to N-7 nitrogen atom of guanine base.

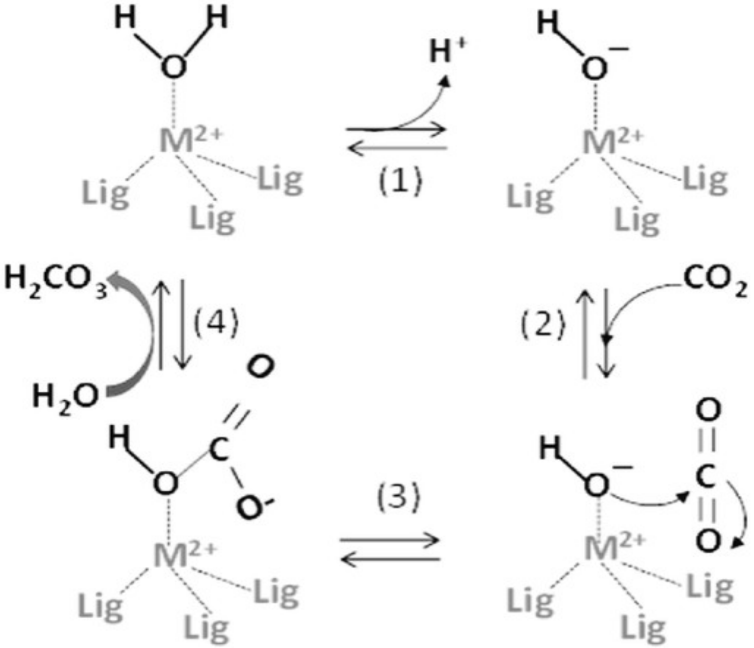
$$\text{cis}-\left[\text{Pt}\left(\text{NH}_3\right)_2\text{Cl}_2\right]+\text{H}_2\text{O}\rightleftharpoons\text{cis}-\left[\text{Pt}\left(\text{NH}_3\right)_2\text{Cl}\left(\text{H}_2\text{O}\right)\right]^{+}+\text{Cl}^{-}$$

$$\longrightarrow\text{cis}-\left[\text{Pt}\left(\text{NH}_3\right)_2\text{Cl}\right]-\text{N}\left(\text{DNA}\right)\xrightleftharpoons[-\text{Cl}^{-}]{+\text{H}_2\text{O}}$$

$$\text{cis}-\left[\text{Pt}\left(\text{NH}_3\right)_2\left(\text{H}_2\text{O}\right)-\text{N}-\text{DNA}\right]\longrightarrow\text{cis}-\left[\text{Pt}\left(\text{NH}_3\right)_2\right]=\text{DNA}$$

41. Correct option is (a)

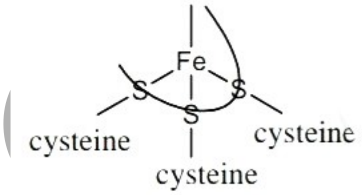
In carbonic anhydrase OH group first attack on CO_2 and then CO_2 interact with Zn.



Here, step (2) shows attack of OH group with CO_2, the product formed after step (3) shows later interaction of CO_2 with Zn metal.

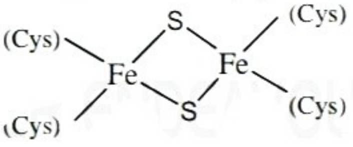
42. Correct option is (a)

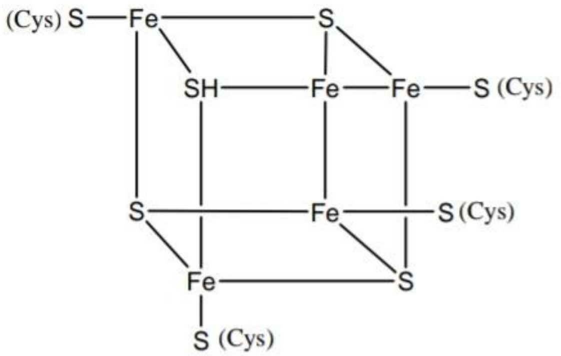
Ruberdoxin cysteine



4-iron ferredoxin

2-iron ferredoxin Fe_2S_2





Number of inorganic sulfur (sulfide) which do not belong to protein chain in ruberdoxin, 2-ferredoxin and 4- ferredoxin are 0, 2, 4 respectively.

43. Correct option is (b)

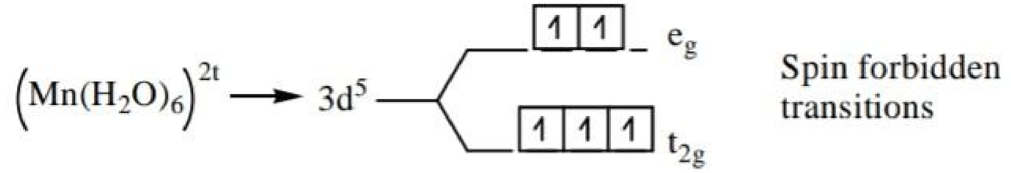
Co-enzyme B_{12} catalyses dehydration, 1, 2-carbon shift reaction in organic substrates and conversion of ribonucleotide to deoxyribonucleotide.

44. Correct option is (c)

Metallothionines → Cystein rich protein
Plastocyanin →Electron Transfer
Ferritin→ Iron storage
Chemotherapy→ Carboplatin

45. Correct option is (b)

Heme A → Iron porphyrin →Colour due to π-π* water splitting enzyme contains bridged Mn_4 cluster

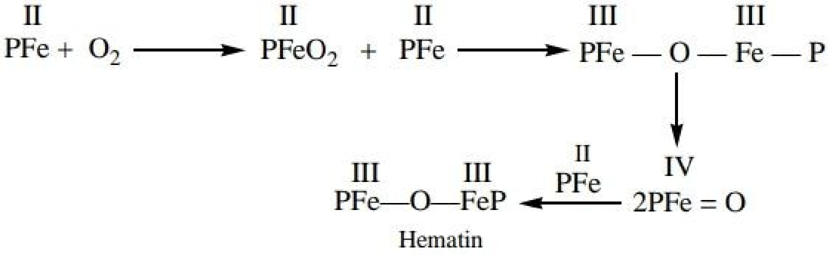


$[Cr(H_2O)]^{+2} \rightarrow t^3_{2g}\ e^1_g \rightarrow$ Tetragonal elongation

46. Correct option is (a)

In oxyhemerythrin $\bar{\upsilon}_{O\text{-}O} = 850\ cm^{-1}$
In oxyhemoglobin $\bar{\upsilon}_{O\text{-}O} = 1100\ cm^{-1}$

47. Correct option is (a).



48. Correct option is (b)

Metallothioneins are cystein rich, low molecular weight protein. Due to soft sulfur centre they prefer to bind.

49. Correct option is (a)

Both deoxyhemerythrin and deoxy hemocyanin are O_2 transport protein in biological system. Both contain two metal ion at active site and they bind only O_2 per active site.

50. Correct option is (c)

Cytochrome-c shows redox reaction and it is an essential component of electron transport chain. whereas it is carriers of one electron and does not bind oxygen

51. Correct option is (c)

In oxyhemerythrin, both the Fe are present as Fe(III) and there is presence of hydrogen bonding and dioxygen bind to only one Fe.

52. Correct option is (d)

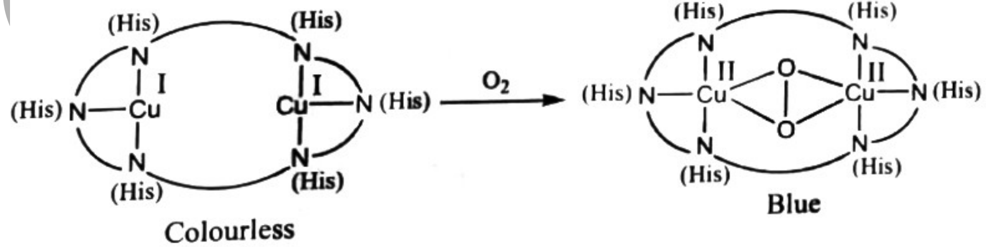
Cubane like ferredoxin is Fe_4S_4 . It has four inorganic sulfide which can be removed by treatment with acid.

$Fe_4S_4 \overset{H+}{\rightarrow} Fe_4^{+8} + 4H_2S$

53. Correct option is (d)

The Cu ion is essential that can not be replaced by other metal atom while retaining activity. On the other hand, the Zn^{+2} ion can be replaced by other divalent metals atom such as Co or Cd with retention of most of the activity.

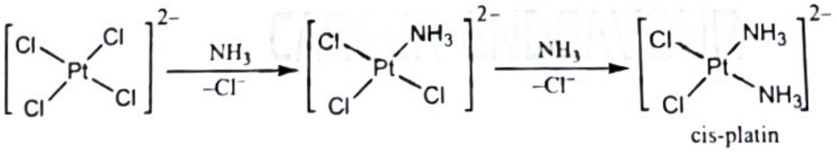
54. Correct option is (d)



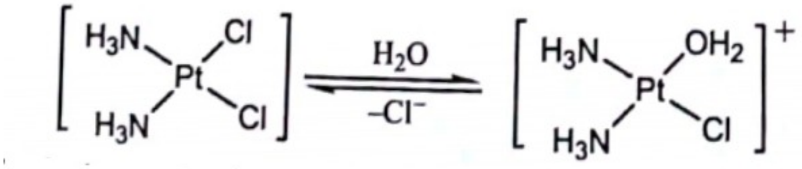
(1) In oxygenation of hemocyanin each Cu atom is oxidized by one.

(II) It becomes intense blue from colourless due to LMCT (O_2^{-2} to Cu^{+2})
(III) O_2 is reduced to O_2^{-2} because each Cu is oxidized by one.
(IV) The O_2^{-2} binds to two Cu atoms in the **μ-η^2 : η^2** manner.

55. Correct option is (a)

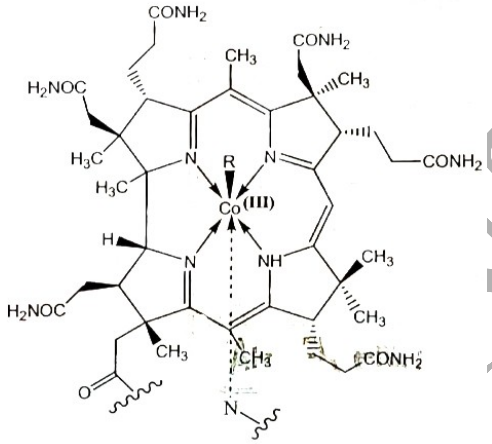


Trans effect of Cl^- > NH_3
In blood it stays in equilibrium with cis-$[Pt(NH_3)_2Cl(H_2O)]^+$



In DNA stand, cis-platin binds to two adjacent guanin bases (Not to cytosine bases)

56. Correct option is (a)



57. Correct option is (a)
Oxymyoglobin → O_2^- →1105 cm^{-1}
Oxyhemocyanin → η^2 : $\eta^2 O_2^{-2}$ →803 cm^{-1}
Oxyhemerythrin → HO_2^- → 844 cm^{-1}

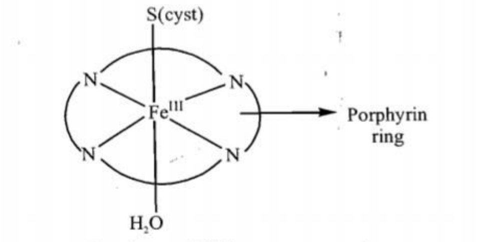
58. Correct option is (c)
Siderophores/siderochromes are small, high-affinity iron-chelating compounds secreted by micro organisms such as bacteria and fungi and serving to transport iron across all membranes.

59. Correct option is (d)
(P) Dichlorodifluoro methane →(iv) Ozone layer depletion
(Q) Sulfadiazine→ (iii)Antibacterial

(R) Cortisone→ (i)Anti-inflammatery
(S) Hexachlorobenzene→ (ii)Insecticidal

60. Correct option is (c)

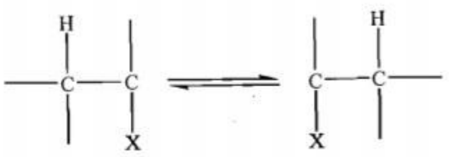
Cytochrome P-450 is a membrane bound metalloenzyme. The function of most cytochrome P-450 enzyme is to catalyze the oxidation of organic substrate. In the active site of cytochrome P-450, iron is in +3 oxidation state and it is in octahedral geometry whereas the basal plane is composed of four N atoms from the porphyrin ring, fifth position is occupied by a cysteine moiety and sixth position is occupied by H_2O molecule.



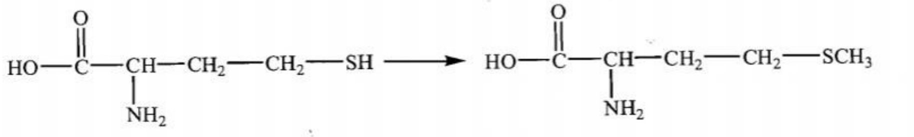
Cytochrome P-450

61. Correct option is (d)

Coenzyme Vit-B_{12} was the first organometallic compound discovered in living systems. This coenzyme catalyses 1, 2-rearrangement.



•Coenzyme B_{12} readily accepts a methyl group or hydroxyl methyl group (bound to Co) that can be transferred to add a carbon to a substrate



$$HO-\overset{O}{\overset{\|}{C}}-\underset{NH_2}{\underset{|}{CH}}-CH_2-CH_2-SH \longrightarrow HO-\overset{O}{\overset{\|}{C}}-\underset{NH_2}{\underset{|}{CH}}-CH_2-CH_2-SCH_3$$

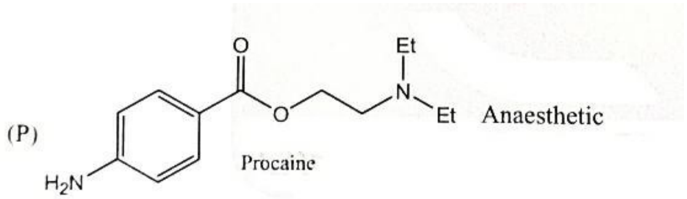
•Coenzyme B_{12} reduces -CH(OH) group to $-CH_2$ group

62. Correct option is (b)

•Both oxymyoglobin and cytochrome P_{450} contain dianion of protoporphyrin-IX.
•Oxymyoglobin has fifth ligand bonded to metal centre from protein hackbone but in cytochrome P_{450} one S-atom of cysteine is coordinated instead of histidine from protein backbone.
•Both contain single active site [Fe (III)]

63. Correct option is (a)

(P)

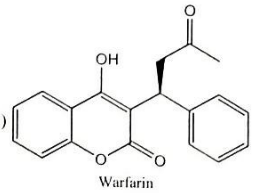


Procaine

Anaesthetic

Procaine is a local anesthetic drug of aminoester group. It is used primarily to reduce the pain of intramuscular injection of penicillin.

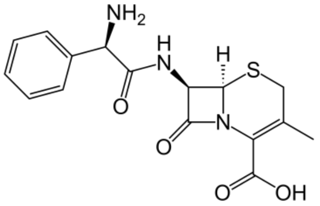
(Q)



Warfarin

Anticoagulant

Warfarin is used as an anticoagulant. It is commonly used to treat blood clots such as deep vein thrombosis and pulmonary embolism and to prevent stroke in people who have atrial fibrillation values heart diseases as artificial heat value.



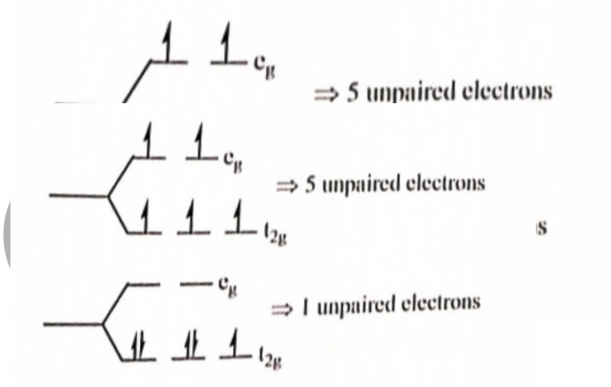
Cefalexin, also spelled cephalexin, is an antibiotic that can treat a number of bacterial infections. It kills gram-positive and same gram-negative bacteria by dissrupting the growth of the bacterial cell wall. Cefalexin is a beta-lactam antibiotic within the class of first-generation cephalosposins.

64. Correct option is (b)

In oxymyoglobin, Fe^{+3} present in low spin. Thus, have configuration t_{2g}^5 e_g^0 i.e one unpaired electron.

$[Fe(ox)_3]^{3-}$

$Fe^{+3} = 3d^5$



(C) $[NiCl_4]^{2-}$

Ni^{+2} = d^8 = t_{2g}^4 e_g^4

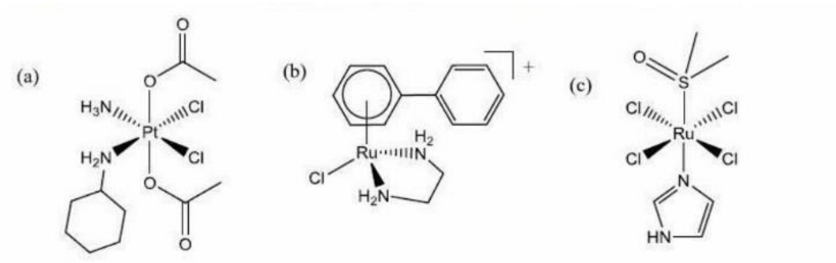
2 unpaired electron

(D) **$[Cu(NH_3)_4]^{2+}$**
Cu^{+2} $= t_{2g}^5\ e_g^4$
1 unpaired electron

65. Correct option is (a)

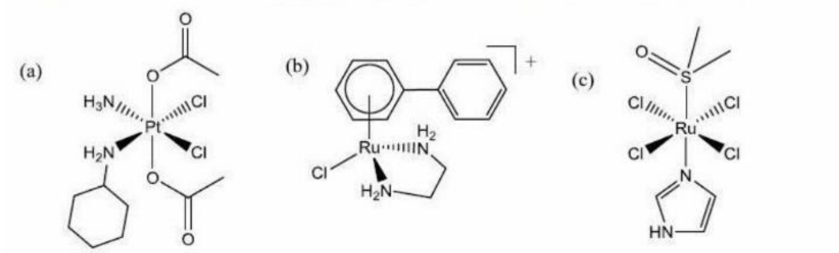
(A) Ni present in coenzyme F_{450} (III) which catalyzes the release of methane (Y) in the final step of methanogenesis.
(B) Zn present in carbonic anhydrase (I) which catalyses the hydration of CO_2 into H_2CO_3 (Z).
(C) Mo present in Xanthine oxidase (II) which catalyzes the oxidation of Xanthine to uric acid (X).

66. Correct option is (d)

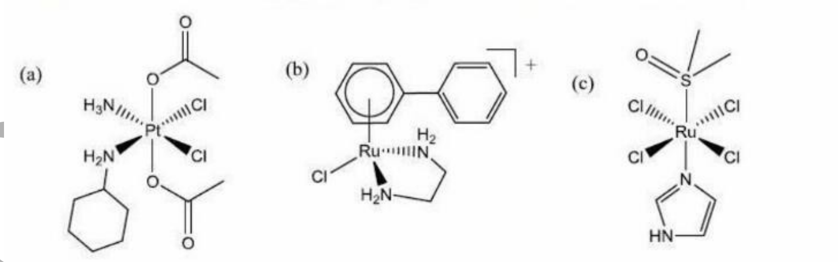


It is an orally active antitumor agent. Its action seems to be similar to that of Cisplatin, but with the added feature that its ligands protect it from reaction in digestive system and allow it to be absorbed into blood stream.

•Glutathione (GHS) is capable of preventing damage to important cellular components caused by reactive oxygen species



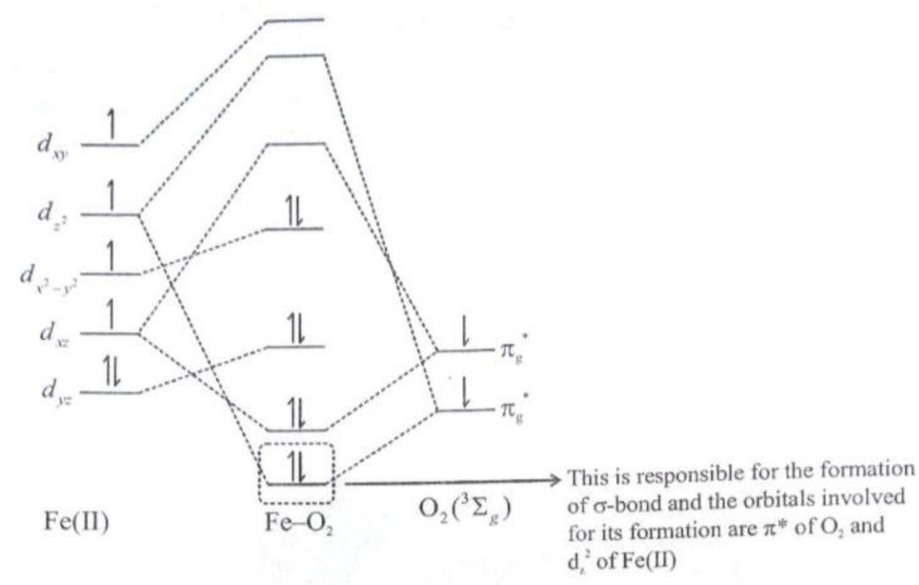
has promising anticancer activity as it binds to GSH and when followed by oxidation, promotes binding to guanine in DNA.



shows anti-metastatic action as instead of binding with DNA, it interacts with actin type proteins on cell surface or with collagens of extra-cellular matrix, which leads to reduced mobility of invasive cancer cells,

67. Correct option is (a)

The molecular orbital diagram for binding of O_2 to myoglobin is


d_{xy}
d_{z^2}
$d_{x^2-y^2}$
d_{xz}
d_{yz}
π_g^*
π_g^*
Fe(II)
Fe–O$_2$
O$_2$($^3\Sigma_g$)
This is responsible for the formation of σ-bond and the orbitals involved for its formation are π* of O$_2$ and d_z^2 of Fe(II)

ts formation are π* of O_2 and d_z^2 of Fe(II)

68. Correct option is (d)

In the catalytic cycle of cytochrome P_{450}, peroxo complex [(porphyrin)Fe^{III}(OOH)] undergoes protonation which leads to removal of one oxide ion as water via heterolytic O-O cleavage to form oxyferryl complex with one electron having been oxidized from **π** -HOMO of porphyrin ring leaving it as a radical cation i.e. **[(porphyrin)$^{+\bullet}$Fe^{IV}(O)]**

69. Correct option (c)

Zeolite is used for capturing CO_2,

Indium tin oxide (ITO) is a form of perovskite used in solar cells.

LiCoO2, Lithium cobalt oxide is a dark blue or bluish-gray crystalline solid, and is commonly used in the positive electrodes of lithium-ion batteries

Pt alloy is used in fuel cells. Pt is used as the catalyst for both the hydrogen oxidation reaction (HOR) occurring at the anode and the oxygen reduction reaction (ORR) at the cathode.

70. Correct option (a)

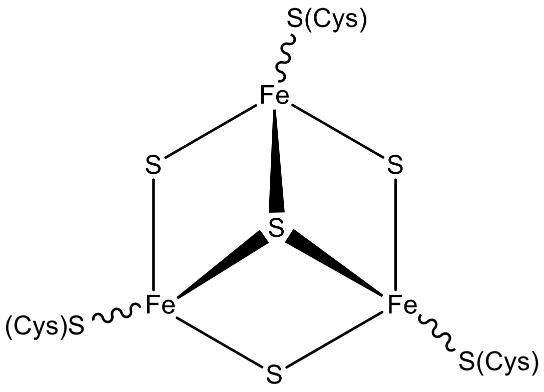
Biological function of Hemerythrin and Hemocyanin is O_2 transport.

Cytochrome P450 and Tyrosinase are Oxygenase

Rieske Protein and Azurin are used for electron transfer.

71. Correct option (a)

In 3-iron ferredoxins, the number of sulfide bridges is 3 and cysteinyl ligands are also 3



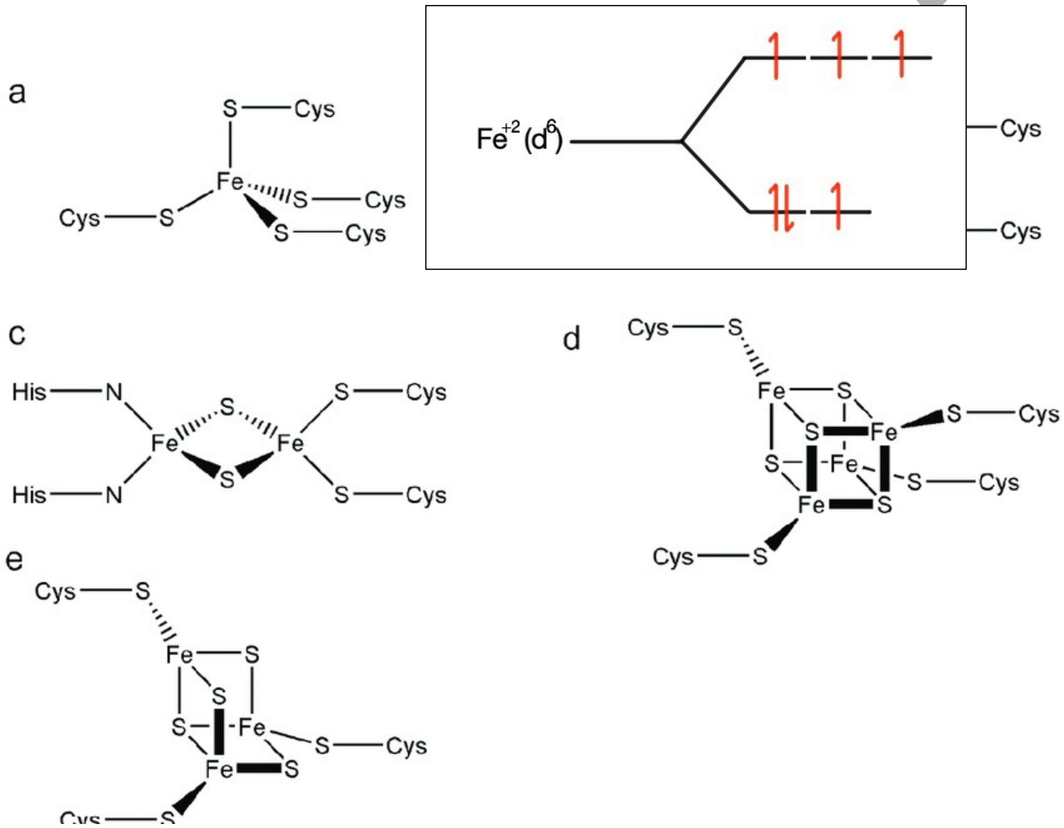
72. Correct option (d)

Rubredoxin consist of Fe^{+2} centre with Tetrahedral geometry, hence statement (A) is correct.

Reduced form of iron is paramagnetic in nature, statement (B) incorrect.

Due to presence of asymmetric electrons in eg orbitals, Jahn-Teller distortion is observed. Thus statement (C) is correct.

Rubredoxins are [1Fe–4S] clusters, hence statement (D) is incorrect.



POINT

Analytical Chemistry

Hints & Solutions

1. Correct option is (c)

In inductively coupled plasma atomic emission spectroscopy, the plasma gas flows in a helical pattern (i.e. induction coil) which provides stability and helps to late thermally the outside quartz tube.

2. Correct option is (a)

In thermometric titration, the determinant of the degree to which a reaction will proceed to completion is the free energy change, which must be favourable. Other condition to obtain best result in thermometric titration are

- The reaction should be accompanied by sufficient heat change.
- Heat of dilution should be negligible
- Reaction should be a simple one step changed
- Transfer on heat between the titration vessels and its surrounding should be avoided.

3. Correct option is (c)

- The hollow cathode lamp is an excellent, having highest sensitivity, bright line source for most of the elements determinable by atomic absorption.
- The most advanced and widely used high sensitivity sampling technique for atomic absorption is the graphite furnace. Detection limit for the graphite furnace fall in the ng/L range for most elements. The sample is atomised in a very short period of time, concentrating the available atoms in the heated cell and resulting in the observed increased sensitivity.

4. Correct option is (c)

(a) In spectrofluorimetry the wavelength of incident light can range from 200 nm to 900 nm.

(b) Intensity and colour of the fluorescence of many substance depends upon the pH of solutions.

(c) Since, presence of O_2 decreases the fluorescence, thus oxygen is eradicated from the solution.

(d) In flourimetry absorbance of analyte solution is generally kept near to 0.05.

5. Correct option is (a)

- In conductometric titration the end point of titration is determined by means of conductivity measurements. For example, via conductance/resistance vs volume of alkali plot.
- Amperometric titration refers to a class of titrations in which the equivalence point is determined through measurement of the electric current produced by the titration reaction.
- Differential pulse polarography is an electrochemical technique where the cell current is measured as a function of time and as a function the potential between the indicator and reference electrodes.

6. Correct option is (b)

H_3PO_4 is used in the estimation of Fe(II) with $K_2Cr_2O_7$ using diphenylamine sulphonate as indictor to reduce the electrode potential for the $Fe^{+3} \rightarrow Fe^{+2}$ reaction by stabilising the ferric ion.

7. Correct option is (d)

•Copper (Cu), Silver (Ag) and Gold (Au) are called currency metal (present in native form). Amperometric titration is the one of the economic technique for estimation of these metals.

• It is a class of titration in which the equivalence point is determine through measurement of electric current produced by the titration reaction.

• Amperometric titration sensitivity is always higher than than those of spectrophotometeric titrations.

•Amperometric titration does not generally require an indicator.

•Amperometric titration does not require inert atmosphere.

8. Correct option is (a)

Thermometric titration is the method in which a titrant is added stepwise to a vessel containing another reactant. The enthalpy change on heat of reaction causes a temperature change which when plotted versus volume of titrant is used to detect the end point.

(i) Electron capture detector is a device for detecting atoms and molecules in a gas and is used in atoms and molecules in a gas and is used in Gas-liquid chromatography.

(ii) The abnormal peak which appears in polographic titration can be supposed by addition of Gelatin.

(iii)In spectrofluorimetry laser may used as source.

9. Correct option is (a)

A commonly used measure of the separating efficiency of a column is height equivalent theoretically plate (HETP). It can be determined by van Deemter equation.

HETP depends upon

- Mean carrier gas velocity
- Temperature of the column
- Packing of the column

HETP does not depends upon particle size

10. Correct option is (b)

Electron diffraction is used to get the bond parameters of gaseous samples

11. Correct option is (c)

(a) Oxalic acid versus potassium permanganate:
End-point is colorless → pink purple (λ_{max} = 525 nm)
(b) Iron (II) versus 1, 10-phenanthroline:
End-point is colorless → Reddish-orange (λ_{max} =512 nm)
(d) Nickel (II) versus Dimethylglyoxime:
End-point is colorless Red (λ_{max} = 445 nm)
(c) Cobalt (II) versus Eriochrome Black-T:
End-point is Blue-green → green
(pH=8) (λ_{max} =660 nm) (λ_{max} =600 nm)
Free EBT → Co(II) + EBT complex
Since, color change at end-point is not significant for option(c) which is requirement of the spectrophotometric titration. Therefore, color monitoring method is not suitable in this case.

12. Correct option is (d)

The peak area of differential thermal analysis is proportional to
(i)mass of the sample
(ii) heat of decompositional phase change

13. Correct option is (b)

Phosphorescence has been observed form a wide variety of compounds and is differentiated from fluorescence by long lived emission of light after extinction of the excitation source i.e. it done after fluorescence, if parsists.
Phosphorescence increases when heavy atoms like iodine silver and lead etc. are added.
Phosphorescence increases, when analyte used become immobile.
Hence, both (A) and (B) are correct.

14. Correct option is (b)

Correct statement are
•Area of different thermal analysis peak is proportional to amount of sample
•In the thermo gravimetric analysis area of curve is proportional to mass loss
•In thermo gravimetric analysis two metal ion simultaneously determine.

15. Correct option is (d)

Primary analytical method is isotopic dilution mass spectrometry (not using a reference).

16. Correct option is (c)

Decomposition temperature of $CaCO_3$ in thermogravimetric analysis will be highest in dynamic atomosphere due to the presence of 1:1 mixture of O_2 and CO.

17. Correct option is (a)

Coulometry is based on Faraday's law of electrolysis

18. Correct option is (a)

Inductively coupled plasma atomic spectroscopy (ICP-AES) is an analytic technique used for detection for trace metals and it is better than AAS for simultaneous determination of metal ions. Hence, option (d) is correct.
In Atomic Absorption Spectroscopy mercury lamp is not suitable source but hollow cathode lamp (HCI) are the most common radiation source in Atomic Absorption Spectroscopy and atomizers most commonly used are flame and electro thermal (graphite). Solid sample is used in determination.

19. Correct option is (a)
Thermometric titration is the method in which a titrant is added stepwise to a vessel containing another reactant. The enthalpy change on heat of reaction causes a temperature change which when plotted versus volume of titrant is used to detect the end point.
(1) Electron capture detector is a device for detecting atoms and molecules in a gas and is used in atoms and molecules in a gas and is used in Gas-liquid chromatography.
(2) The abnormal peak which appears in polographic titration can be supposed by addition of Gelatin.
(3)In spectrofluorimetry laser may used as source
20. Correct option is (d)
The residual current in case of DCP is non-faradic current which should be minimum to get the accurate result. This problem of non-faradic current is overcome by use of DPP in which non-faradic current is less than DCP. That is why DPP is more sensitive than DCP.
Though the polarograph is different in both cases but it has nothing to do with sensitivity.

21. Correct option is (a)
Increase of intensity of light used increases fluorescence as the fluorescence life-time increases. Molar absorptivity increases absorbance which further enhances fluorescence.

22. Correct answer (a)
For ICP-OES and ICP_MS argon is **most suitable gas to generate plasma**.
A number of gases cane be used to produce plasma, like Ar, Ne, N_2, O_2, H_2, air and mixture of gases. The physical properties of the gases play a decisive role in this regard. Such important properties are ionization and dissociation energy, thermal conductivity, atomic weight and chemical reactivity.
Argon belongs to the group of inert gases. It means that it does not react with the material during production of plasma. Its atomic weight - the highest among all plasma gases and it generates high kinetic energy of the plasma beam. Due to its low ionization potential argon is excellently suitable for generating the plasma beam. However, argon has a low thermal conductivity and a low thermal capacity which limits its application is some specific areas only.

23. Correct answer is (c)
Gel permeation chromatography is a size exclusion chromatography , that separates analytes on the basis of size. So, the size difference in fatty acids and low molecular weight peptides is greater so they can be separated by using gel permeation chromatography.

24. Correct answer is (d)

In thermogravimetric analysis (TGA) use of dynamic innert atmosphere is decrease with respect to temperature.

25. Correct answer is (a)
Statements A, B and C are correct.

26. Correct answer is (b)
Chemical reactions between analyte and matrix that prevent the atomization of the analyte. One common one is that Sulfate or phosphates anions will form non-volatile salts with Fe^{+3}, so its signal decreases. Can be treated in two ways
1. Releasing agents can add to metal to prevent formation of interference complexes. example EDTA or 8-hydroxyquinoline.

27. Correct answer: (d)
(a) O_2 must be removed as it give its own polarogram, due to following reactions,
$O_2 + 2H^+ + 2e^- = H_2O$; $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
(b) Dropping mercury electrode is the working electrode
(c) $I_d \propto C$
(d) Residual current need not to be made zero.

28. Correct answer is (c)